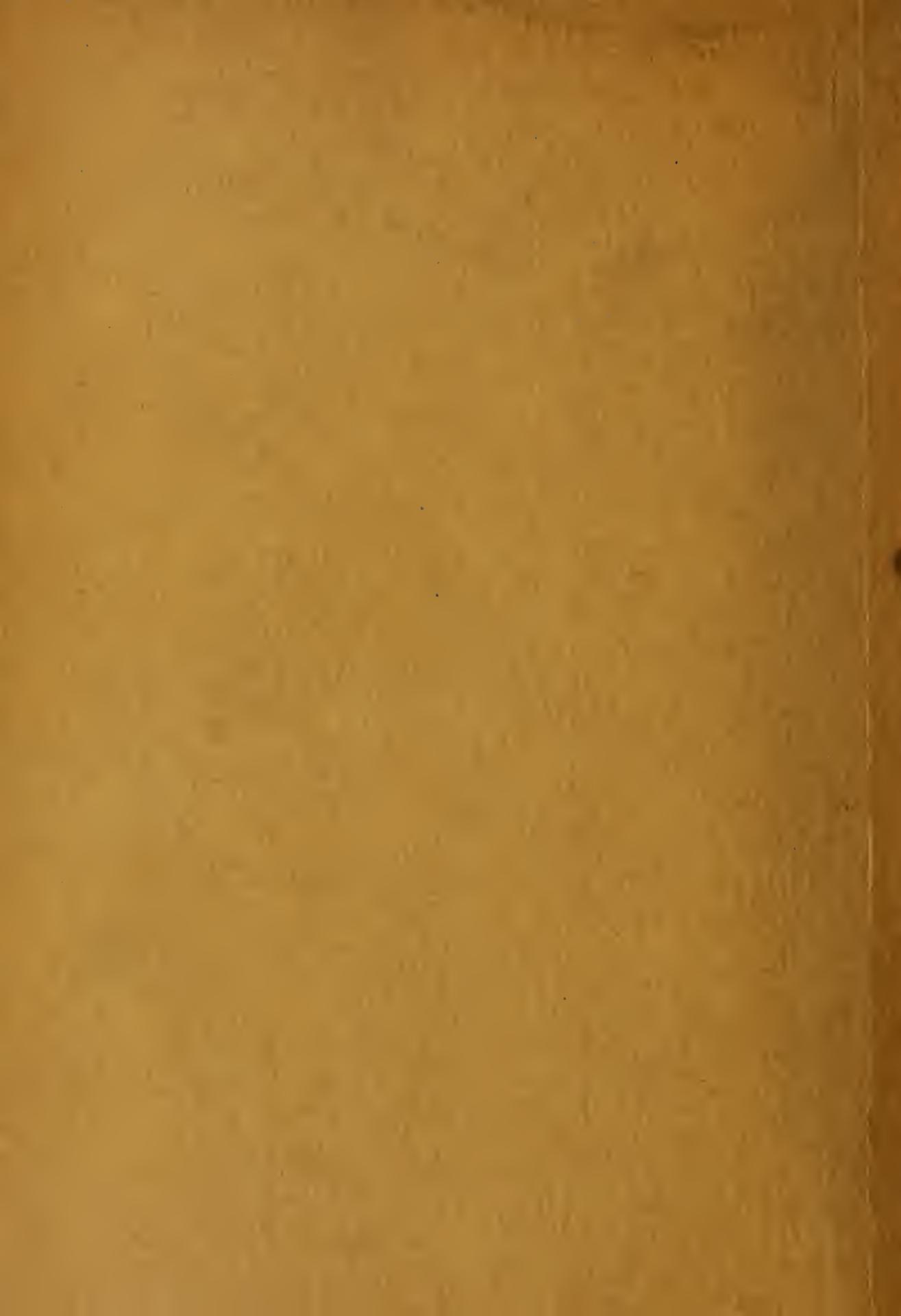


1916  
B21



HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS  
AND METALLIC SOLUTIONS

THE INTERACTION OF MIXED SALT SOLUTIONS  
AND LIQUID AMALGAMS

A STUDY OF THE IONIZATION RELATIONS OF  
SODIUM AND POTASSIUM CHLORIDES  
AND SULPHATES IN MIXTURES

BY

THEODORE ROLLY BALL

B.S. Drake University, 1908  
M.S. University of Illinois, 1914

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THESIS

Submitted in Partial Fulfillment of the Requirements for the  
Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1916



UNIVERSITY OF ILLINOIS  
THE GRADUATE SCHOOL

May 5, 1916

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-  
VISION BY Theodore Rolly Ball

ENTITLED Heterogeneous Equilibria Between Aqueous and Metallic  
Solutions. The Interaction of Mixed Salt Solutions and Liquid  
Amalgams. A Study of the Ionization Relations of Sodium and  
Potassium Chlorides and Sulphates in Mixtures.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE  
DEGREE OF DOCTOR OF PHILOSOPHY.

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Committee

on

Final Examination\*

\*Required for doctor's degree but not for master's.



1916  
B21

I.

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ACKNOWLEDGEMENT.



This investigation was undertaken at the suggestion of Dr. G. McP. Smith and was carried out under his direction. I deem it a privilege to have been associated with a man of such broad scientific knowledge and I take this opportunity to thank him for the many helpful suggestions which he has given during the pursuance of this study.



## I. INTRODUCTION

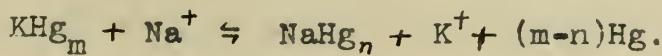
1. Purpose of the Investigation.- This investigation is one of a number that are being carried out in this laboratory, having for their object the study of the ionic relationships which exist in solutions of mixed salts. The present work comprises a study of the chlorides and sulphates of sodium and potassium in total concentrations ranging from 0.20 normal to 2.0 normal, the object being to throw light upon the ionic relationships which exist in mixtures of sodium and potassium salts, whether with or without a common ion. The method used is that developed by G.McP.Smith (1), involving the equilibrium between mixed sodium and potassium salts and liquid amalgams.

2. Principles Relating to the Ionization of Salts in Mixtures.-  
(a) Salts with a Common Ion.- Studies of the ionization of salts, by conductance methods, have led to the conclusion that salts of the same ionic type are ionized to the same extent. (2). Moreover, "It has been shown that the conductance of a mixture of salts with a common ion corresponds to the value calculated on the assumption that the degree of ionization of each salt in the mixture is the same as that which it has when present alone in a solution in which its positive or negative ions have a concentration equivalent to that of the common ion in the mixture". (3) This principle has been further tested by conductance methods by MacGregor, McIntosh, Archibald and McKay (4) and found to be valid "not only for univalent salts but also for those of higher types, even in cases where the mass law would require a very different effect". (3). G.J.M.Mackay (5) has studied this principle by means of transference experiments on a mixed solution of  $KCl$  and  $K_2SO_4$  which was



0.2009 normal with respect to each salt. Assuming that the transference number of the chlorine in KCl in this mixture is the same (0.504) as it is in dilute KCl solutions, the portion of the current carried by the ions from the KCl is 0.573 and that carried by the ions from the  $K_2SO_4$  is 0.427. Multiplying these values by the measured specific conductance of the mixture, the partial specific conductance of each salt in the mixture was obtained. That of the KCl was found to be 2.0% larger and that of the  $K_2SO_4$  5.2% smaller than that required by the principle. Therefore Mackay says that "The principle of ionization in mixtures is subject to serious inaccuracy." It is significant that the ratio of the partial conductances of the two salts is 7.5% larger than the principle requires, yet the observed conductance of the mixture differs from the sum of the calculated partial conductances by only about 1.0%. In the light of the conductance data alone, therefore, the above mentioned principle would seem to be valid; but when the transference data also are taken into account, they point to the conclusion that the agreement of the conductance data with the principle referred to may be due only to an accidental compensation of errors, and that the principle itself is open to serious question.

G. McP. Smith (6) has tested this principle with solutions as concentrated as 1.25 and 1.50 normal. He based his calculations upon equilibrium data obtained from the reversible reaction:



He says, "It follows roughly, that in mixed sodium and potassium chloride solutions, the ratios which exist between the relative ion concentrations of sodium and potassium in the different solutions are identical with those which exist between the relative molal



concentrations of the two salts in the respective solutions." That is to say:

$$\frac{(\text{Na}^+)_1}{(\text{K}^+)_1} : \frac{(\text{Na}^+)_2}{(\text{K}^+)_2} = \frac{(\text{Total NaCl})_1}{(\text{Total KCl})_1} : \frac{(\text{Total NaCl})_2}{(\text{Total KCl})_2},$$

where the subscripts 1 and 2 refer to solutions 1 and 2, respectively. Then he states the isohydric principle of Arrhenius and adds: "The present investigation offers, through an independent method, a striking confirmation of the above conclusions, and moreover, it shows that they hold good even in very concentrated solutions". However, in a later paper by the same author (1) much more <sup>data</sup> covering a wider range of concentration was given. It was shown that in equivalent mixtures of sodium and potassium chlorides and sulphates, in which the total concentration ranged from 0.20 normal to 2.0 normal, the ion fraction of the potassium decreased with increasing salt concentration. At 2.0 normal the ion fraction of the potassium is only 0.456. This is about 9.0% lower than the isohydric principle would require.

(b) Salts Without a Common Ion.- Miles S. Sherrill (7) has studied the ionization of salts without a common ion by conductance methods. He used varicus mixtures of KCl and  $\text{Na}_2\text{SO}_4$  with total concentrations of 0.10 normal and 0.20 normal, at 18°C. He developed a series of equations by means of which he was able to calculate the ion, and also the total undissociated salt concentrations in the mixtures. His calculations were based upon the assumption that for each salt in the mixture, the ratio of the product of the ion concentrations,  $(\text{A}^+)(\text{B}^-)$ , to the undissociated salt concentration,  $(\text{A}_x \text{B}_y)$ , is a function of the total ion concentration of the mixture. This function he shows to be

$$\frac{(\text{A}^+)(\text{B}^-)}{(\text{A}_x \text{B}_y)} = K(\sum i)^{2-\eta},$$



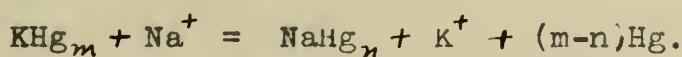
where  $K$  and  $n$  are constants. " $n$ " is empirical and has a value between 1.4 and 1.55 depending upon the salt. (8). From these ion concentrations, Sherrill calculated the equivalent conductances of the mixtures and found them to agree with the observed values within 0.50% in 0.20 normal solutions and within 0.25% in 0.10 normal solutions. But he adds, "The possibility must of course be recognized, that a compensation takes place, owing to the un-ionized tri-ionic salt being present in larger or smaller proportions than that calculated. This might be the case, for example, if the ionization relations of the di-ionic and tri-ionic salts were determined by a different principle and not by the same principle, as has been assumed. All that can be said is that there are at present no facts known that make necessary this more complicated assumption."

In Washburn's "Principles of Physical Chemistry", page 295, we find this statement: "Very recently Kraus has suggested" (in a private communication to the author) "another principle for calculating the degrees of ionization in mixtures. This principle is based upon the assumption that the ionization of a strong electrolyte is determined by the product of the concentrations of its own ions in the solution instead of by the total ion concentration of the solution. On this basis the degree of ionization of a strong electrolyte in any mixture, where its ion product is " $I$ ", is the same as its degree of ionization in its own pure solution at such a concentration that its ion product is " $I$ ". A careful search of the late literature has resulted in a failure to find this work of Kraus.



## II. THEORETICAL.

When a liquid potassium amalgam is placed in a sodium salt solution, the potassium, because of its solution pressure, tends to pass into the ionic state, and there results a difference of potential between the amalgam and the solution. The amalgam becomes negatively charged and attracts the positive ions of the solution. Theoretically one of two things will happen: either the potassium will continue to pass into the solution until the attractive force between the potassium ions and the amalgam, due to the electrostatic charges, becomes equal to the solution pressure of the potassium in the amalgam, or some other positive ions will be forced out of the solution before the above equilibrium can be reached. In the case under consideration, assuming that there is no reaction between the water and the amalgam, sodium ions will be forced into the amalgam until the solution pressure of the sodium becomes great enough to prevent the entrance into the amalgam of any more sodium from the solution. At this point an equilibrium will exist between the sodium and potassium in the amalgam and the sodium and potassium ions in the solution. On the other hand, upon starting with a sodium amalgam and a potassium salt solution, the sodium will pass into the ionic condition and in so doing displace potassium in equivalent quantities from the solution, until the reaction is stopped by the attainment of the same equilibrium. The reaction may, therefore, be written reversibly, as follows:



If mercury is present in large excess, so that its concentration may be regarded as constant, the reaction is one of the second order and, for equilibrium, the mass law expression may be written as follows:



$$\frac{(KHg_m) (Na^+)}{(NaHg_n) (K^+)} = C_o. \quad 1.$$

It is not possible at present to tell the actual ion concentrations of a solution of this kind. But in any solution of a mixture of sodium and potassium salts the ion concentrations must be some function of the respective salt concentrations. That is to say:

$$\frac{(Na^+)}{(K^+)} = n \frac{(Na \text{ salt})}{(K \text{ salt})}. \quad 2.$$

Unless it be true that each salt is ionized to the same extent, we know nothing as to the value of "n". It may be constant for all solutions or it may vary with the total concentrations of the mixtures.

Again it may vary with the ratio between the salts at all concentrations.

But in the case of highly ionized salts, like those under consideration, in very dilute solutions in which the salts are almost completely ionized, the value of "n" must necessarily approach unity.

At infinite dilution it must be equal to unity. In the event of "n" becoming equal to unity, equation 1. may be written,

$$\frac{(KHg_m) (Na \text{ salt})_o}{(NaHg_n) (K \text{ salt})_o} = C_o, \quad 3.$$

where the subscript "o" indicates that the solution of the mixed salts is infinitely dilute.

Now for any solution of mixed salts at a concentration "c" we may write:

$$\frac{(KHg_m) (Na \text{ salt})_c}{(NaHg_n) (K \text{ salt})_c} = C_c. \quad 4.$$

But  $C_c$  does not equal  $C_o$  unless "n" equals unity under the conditions.

Since the reaction under consideration is undoubtedly an ionic



reaction, we should be able to derive the value of  $C_o$  from the expression,

$$\frac{(KHg_m) (Na^+)_c}{(NaHg_n) (K^+)_c} = C_o, \quad 5.$$

if we but knew the values of the ion concentrations.

By dividing equation 5 by equation 4 we get:

$$\frac{(Na^+)_c}{(K^+)_c} \times \frac{(K \text{ salt})_c}{(Na \text{ salt})_c} = \frac{C_o}{C_c} \quad 6,$$

or,

$$\frac{(Na^+)_c}{(K^+)_c} = \frac{C_o}{C_c} \times \frac{(Na \text{ salt})_c}{(K \text{ salt})_c} \quad 6.$$

If the concentrations are expressed in terms of ion fractions, then

$$(Na^+) + (K^+) = 1. \quad 7.$$

From these two equations, if we knew the values of  $C_c$  and  $C_o$ , we could calculate the ion fractions of sodium and potassium in solutions of any salt concentration "c". The value of  $C_o$  cannot be determined directly, but the value of  $C_c$  can be readily calculated from the experimental data by means of equation 4. (page 6) By shaking either a sodium or a potassium amalgam with successive portions of a mixed sodium and potassium salt solution of known composition and of a total concentration "c", until the amalgam each time has come to equilibrium with the solution, it is finally necessary to analyze only the amalgam in order to be able to calculate the value of  $C_c$ . By determining the values of  $C_c$  for a number of different total salt concentrations, and by plotting these values against the total concentrations, it is possible to obtain a curve which will enable us, by extrapolation to zero concentration, to arrive at the value of  $C_o$ , since  $C_o$  is but the limiting value of  $C_c$ .



as the solution becomes more and more dilute.

Unless it should prove that the values of  $C_c$  are independent of the ratios in which the salts are present to give the total concentration "c", all of the plotted values of  $C_c$  would have to be determined with the use of solutions containing the two salts always in the same ratio. Having established a value of  $C_o$  for salts mixed in a definite ratio, and knowing the value of  $C_c$ , we are then in a position to calculate the ion ~~fraction~~ fractions of the sodium and potassium in the solution of total salt concentration "c".

By solving equations 6 and 7 we get:

$$\frac{(K^+)_c \cdot C_o \cdot (\text{Na salt})_c}{C_c \cdot (\text{K salt})_c} = 1 - (K)_c$$

from which it follows that:

$$(K^+)_c = \frac{C_c (\text{K salt})_c}{C_o (\text{Na salt})_c + C_c (\text{K salt})_c} \quad 8.$$

For those cases in which, at equilibrium, the salts are present in equivalent quantities, the formula reduces to the simple form;

$$(K^+)_c = \frac{C_c}{C_o + C_c} \quad 9.$$

G.McP.Smith (1) has developed a formula in terms of the concentrations of the alkali metals in the amalgams, by means of which the ion fractions of the sodium and potassium in the solution may be calculated. The equation is

$$(K^+)_c = \frac{(KHg_m)_c}{(KHg_m)_c + C_o (NaHg_n)_c}$$

In this case, however, formula 9 above, has the advantage of being expressed in terms of  $C_o$  and  $C_c$  alone. Throughout this investigation the agreement which exists among the values of  $C_c$ , which have



been obtained under any given experimental conditions, has been used as a check upon the accuracy of the work. These values are in all cases readily accessible in the tables which follow.



## III.

## MATERIALS AND EXPERIMENTAL METHODS.

## 1. Materials.

It is necessary that the water, salts and mercury used in this work be exceptionally pure, since the presence of even slight traces of heavy metals (9) (10), catalyzes the decomposition of alkali metal amalgams by the water.

## Water.

The water used in these determinations was prepared by distilling the laboratory distilled water successively from alkaline potassium permanganate and dilute sulphuric acid. The distilling flasks were fitted with safety distilling bulbs to prevent spray being carried over. At one time it was thought that some acid was being carried over and in consequence of this the distillate from the acid was redistilled. Glass condensers were used in these distillations, since it was feared that if tin were used colloidal tin might contaminate the water and catalyze the decomposition of the amalgams.

## Salts.

All of the salts used were very carefully purified by recrystallization or precipitation. The mother liquor was removed as completely as possible by suction at the water pump, after which the remainder was thrown off in a high speed electrical centrifuge. In all cases the crystallizations were carried out in vessels of Jena glass, and with the exception of the final one, which was made from the special water, the crystallizations were made from the distilled water of the laboratory.

Sodium Chloride- Commercial NaCl was dissolved in distilled water and the saturated solution filtered through paper in a Buchner funnel. The salt was then precipitated with gaseous HCl and



and treated as described in the preceding paragraph. Two precipitations were made, after which the salt was placed in an open dish and heated on the electric hot plate until the odor of HCl was removed. Just before use the salt was either fused or it was kept for at least an hour at a temperature just short of fusion, in a platinum dish in the electric muffle furnace. It was cooled in a desiccator over calcium chloride.

Potassium Chloride. Sample I. Baker and Adamson's analyzed salt was recrystallized three times from hot water.

Sample II. Kahlbaum's best salt was recrystallized twice. The samples were dried in an electric oven at  $150^{\circ}\text{C}$ , but before use they were finally heated in the same manner as the sodium chloride. No difference could be observed in the action of the two samples so no distinction will be made in the tables as to which preparation was used.

Sodium Sulphate.- Sample I. Kahlbaum's best salt was recrystallized twice from hot water. The crystal water was removed by heating the salt in a large platinum dish in the electric oven, the temperature of which was raised gradually to prevent creeping. When the salt appeared to be dry it was bottled. It was finally dried in a muffle furnace at  $500^{\circ}\text{C}$ . for at least 12 hours. (11) Sample II. Kahlbaum's salt was recrystallized three times from hot water, after which it was subjected to the treatment just described.

Potassium Sulphate.- Sample I. Kahlbaum's best salt was recrystallized three times from hot water.

Sample II. Kahlbaum's salt (Zur Analyse) was recrystallized once. Before weighing the salt, it was ground to a fine powder in an agate mortar and dried in the muffle for at least four hours at  $500^{\circ}\text{C}$ .



## Chloro-platinic Acid.

Platinum black was dissolved in aqua regia and the resulting solution evaporated alternately with HCl and with water until the diphenylamine test for nitric acid gave a negative result. The acid was then dissolved in water and chlorine gas passed through the solution until it was saturated. The excess of chlorine was completely removed by passing a stream of well washed air through the solution at room temperature. The solution was then diluted until each cubic centimeter contained 0.05 gram of platinum.

The factor to be used with acid prepared in this way was found by taking a known weight of pure fused KCl and converting it into the chloro-platinic acid. 0.1027 gram of KCl and 0.0890 gram <sup>of NaCl</sup> were mixed and then analyzed for potassium, the mixture yielding 0.3369 gram of  $K_2PtCl_6$ . This gives a factor of 0.3048 for KCl. A sample of the potassium salt was prepared from this acid and analyzed for KCl by reducing it in a current of illuminating gas. The KCl was dissolved, filtered from the platinum and weighed. 1.7831 grams of the potassium salt yielded 0.5442 gram of KCl. This gives a factor of 0.3052. The commonly accepted factor is 0.3056. (12) Since 0.3048 differs from 0.3056 by only about 0.2%, and since we were not able to check duplicate determinations of the value of  $C_c$  by less than 1.0%, it evidently makes no difference which value is used; but owing to the fact that 0.3056 is the factor commonly recommended, we have preferred to use it (rather than 0.3050) in all of our calculations.

## Recovery of the Platinum.

Two procedures were used for the recovery of the platinum.  
(a) In the early part of the work the alcoholic residues and the



precipitates were mixed, an excess of KCl solution added and the solution evaporated on the water bath. The residue was then dried in the oven, and after being powdered in an agate, mortar was placed in a combustion tube and the platinum reduced in a current of illuminating gas. The reduced metal was then washed with hot water until the filtrate gave no precipitate with silver nitrate.

(b) The above method was later given up for the more rapid and convenient one of reducing the platinum from an alkaline solution with ammonium formate. Usually no trouble was experienced, but at times a green precipitate was thrown down which was very inert; this was undoubtedly Magnus' Green,  $[(\text{NH}_3)_4\text{Pt}]\text{[PtCl}_4\text{]}$ , which is known to be formed by the action of ammonia upon chloro-platinous acid. (13) When sodium formate was substituted for the ammonium salt this difficulty was removed. The reduced platinum was washed with dilute HCl and finally with water until the filtrate was free from chlorides.

#### Mercury.

Commercial mercury was freed as completely as possible from dregs by passing it through a pin hole filter. It was then shaken in a heavy separatory funnel with a dilute solution of sulphuric acid and potassium dichromate. (14) The mercury was drawn off from the oxide formed, shaken with a fresh portion of the solution and again drawn off. A good deal of oxide came off with the mercury, but this was removed by shaking with dilute nitric acid. The mercury was then poured into a funnel with a capillary outlet, from which it was allowed to run in a very fine stream through a long cylinder filled with a saturated solution of mercurous nitrate in moisture dilute nitric acid. (15) Adhering was absorbed from the mercury



with a filter paper and the metal was then distilled from a 200 c.c. Claisen bulb. in a slow current of air. The flask was attached to an air condenser which extended into a vacuum vessel such as is used for collecting fractions of organic distillates, and which was attached to the water pump. The capillary tube through which the air was drawn extended nearly to the bottom of the flask. The air current was regulated by means of a screw pinch cock on the upper end of the capillary. The air served the double purpose of oxidizing any base metals which might have been present and of preventing bumping. The mercury thus obtained contained some oxide, and to remove this, the mercury was run through the column again. After drying by means of a filter paper, this mercury was used in the preparation of the amalgams.

#### Amalgams.

The amalgams were prepared by electrolysis, as described by G. McP. Smith and H. C. Bennett. (16, About 2.5 kilos. of mercury were placed in a heavy Jena beaker of about 400 c.c. capacity and 50 c.c. of saturated sodium or potassium chloride solution were added. Then the solid salt was added in sufficient quantity to furnish alkali metal enough to give an amalgam of the desired concentration. In this way the solution was still saturated with salt at the end of the electrolysis. The mercury was made the cathode by connection through a column of mercury contained in a glass tube, through the lower end of which a platinum wire was sealed. The anode was a platinum foil (1x2 cm.) welded at an angle of 45° onto the end of a heavy platinum wire; the foil was immersed in the solution almost to the surface of the mercury. A current of from 3 to 4 amperes was used, the E.M.F. being 20 volts



at the cell terminals, and the electrolysis was continued until nearly all of the solid salt had dissolved. When the electrolysis was finished the electrodes were removed and the solution decanted from the mercury. The amalgam was then washed with distilled water several times by decantation and as much of the water as possible was removed with a pipette. The amalgam was then dried by dipping filter papers into it until no trace of moisture could be observed. It was then placed in dry sealing bottles, holding from 500 to 800 grams. The neck of each bottle was then drawn to a capillary and sealed. It was found advisable to open the bottles after an hour or two to let off the pressure, as all traces of moisture could not be removed by the filter paper and this moisture gave rise to a slow evolution of hydrogen.

The amalgams were analyzed, either by decomposing 30 to 40 grams (weighed to the closest centigram) with an excess of 0.10 normal HCl and titrating the excess with 0.10 normal  $\text{Na}_2\text{CO}_3$ , using methyl orange as an indicator, or they were decomposed with HCl, the acid solution evaporated to dryness and the chloride weighed. The concentration which was found most convenient was 0.23% Na and 0.39% K by weight. This concentration, which is <sup>tenth of a</sup> one milligram equivalent of alkali metal per gram of mercury, was sought in each case and most of the amalgams were approximately of this concentration.

The following data will show the efficiency which may be obtained by this method of electrolysis. In the preparation of a sodium amalgam, a mean of 1.42 amperes (This was the first amalgam made; in all other cases 3 to 4 amperes were used.) was passed for 105 minutes. By Faraday's Law,

$$\frac{1.42 \times 105 \times 60 \times 23}{96500}, \text{ or } 2.13 \text{ grams of sodium}$$



should have been deposited upon the mercury. Upon analysis of the amalgam it was found that 1.99 grams of sodium were present. This represents an efficiency of 93%.

In making a potassium amalgam a mean of 3.27 amperes was passed for 54 minutes. This is equivalent to 4.30 grams of potassium, and the analysis showed that 93.3% of this amount had been deposited. (cf. G.McP.Smith and H.C.Bennett (16)) This probably represents the maximum efficiency which we attained. In most cases the amount of current was not recorded, but, as has already been mentioned, the electrolysis was continued until most of the solid salt had dissolved.

## 2. Apparatus.

Thermostat.- A large Freas thermostat holding about 350 liters of water, was used. It was adjusted at  $25^{\circ}\text{C}$ . and was constant within about 0.02 of a degree and accurate within about the same limits.

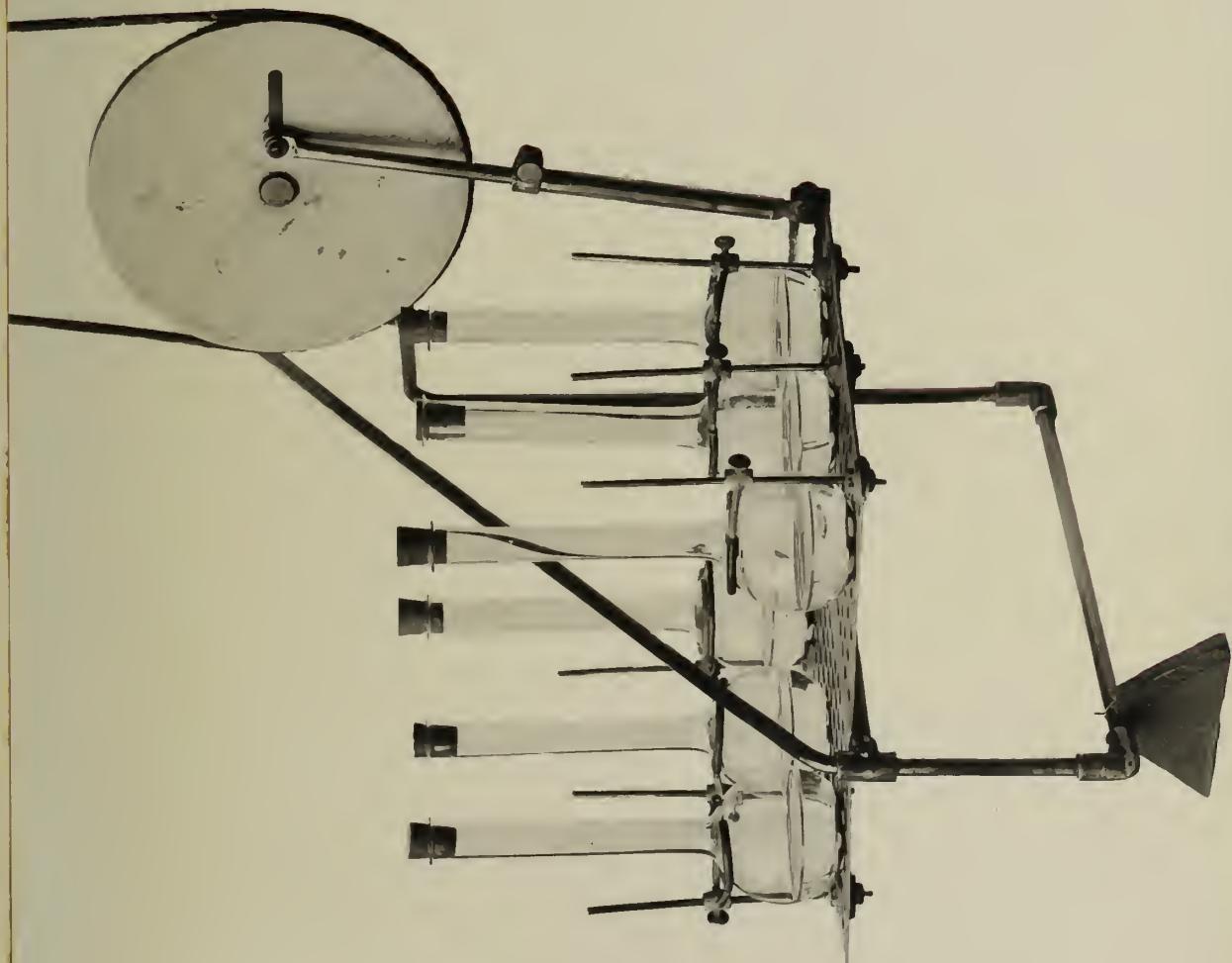
Thermometer.- The thermometer was standardized by comparison with a U.S. Bureau of Standards thermometer which was kindly loaned to us by Dr. Washburn. It was kept in the thermostat all of the time, with the bulb very near the center.

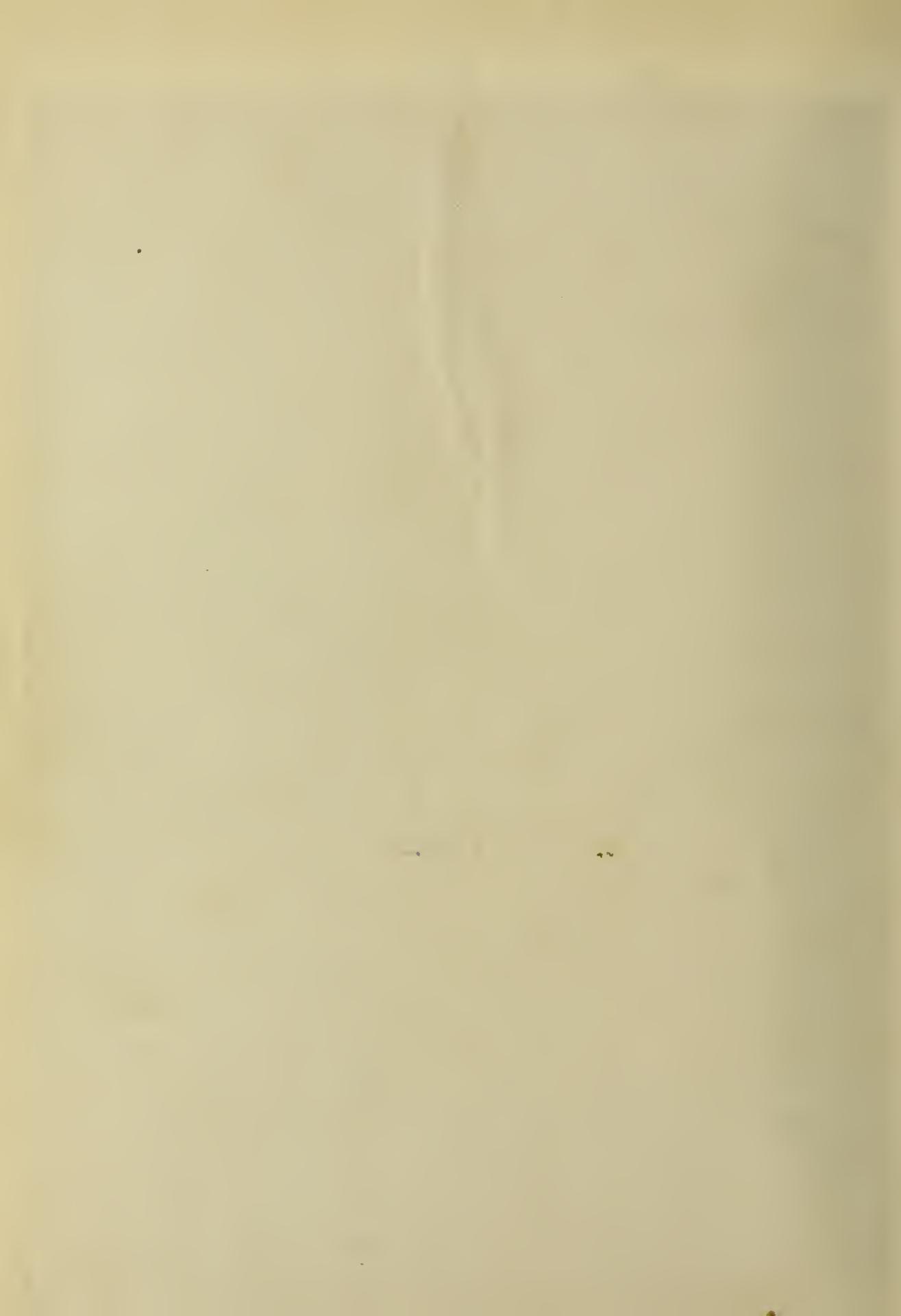
Shaking Device.- The amalgams were agitated in the flasks on the platform of the shaker shown in the accompanying photograph. (Figure I, page 17.) The platform of the apparatus was immersed in the thermostat to such a depth that the surface of water came within about an inch and a half of the top of the flasks when the latter were at their lowest level. The upper end of the apparatus was screwed to the board which supported the lid of the thermostat, while the lower end rested upon a triangular piece of wood which



Figure I  
Shaking Apparatus.

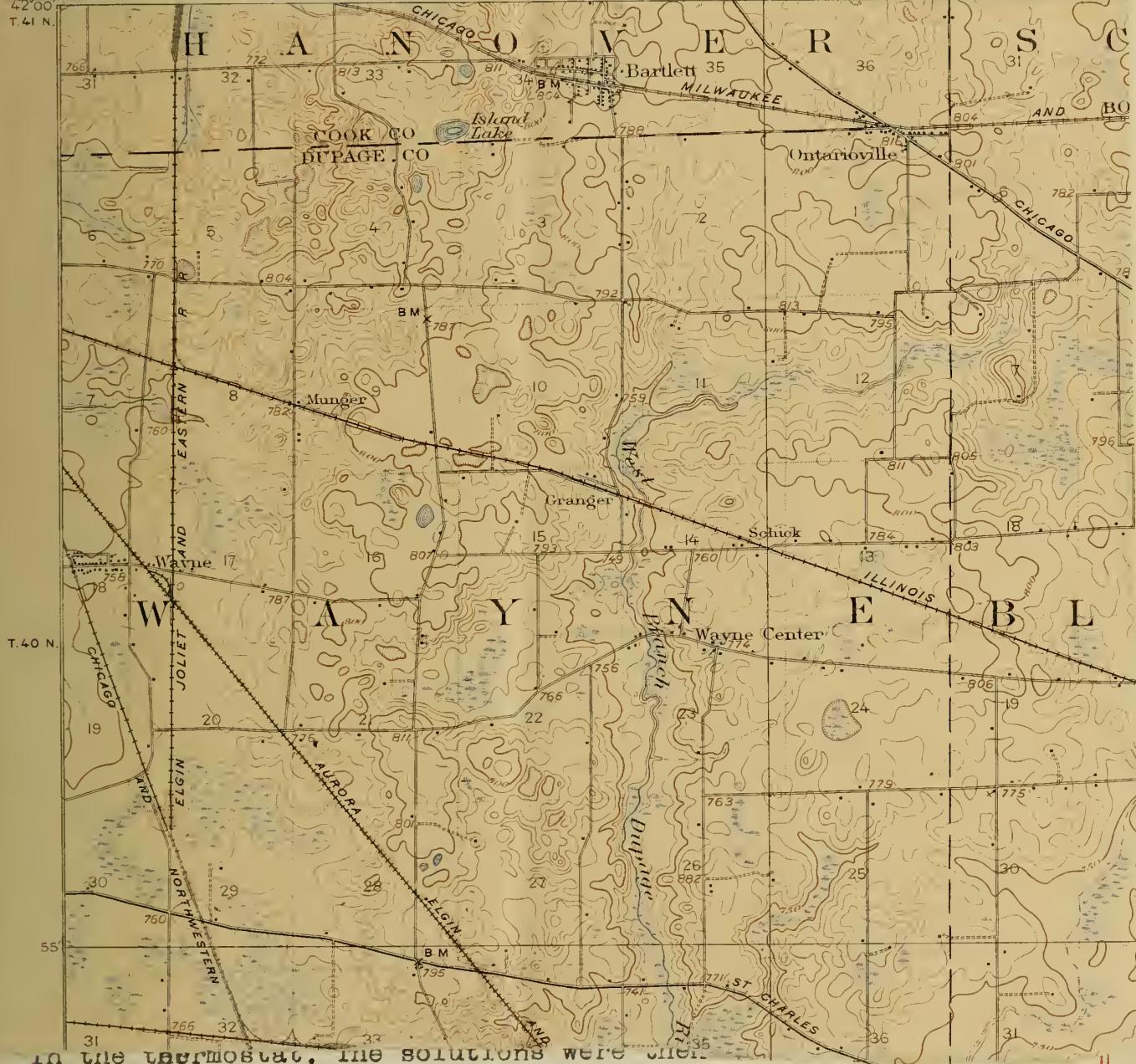
17.





was secured, by means of a copper wire, to the horizontal screen which protects the stirring paddles. The shaker was propelled by an independent motor placed on a shelf above the thermostat. The platform made one complete oscillation per second. By moving the

swirling arm in or out in the slot in the wheel the magnitude of



in the thermostat. The solutions were then

of "Resistenz" glass. Whenever a large number of determinations were to be made at the same total concentration, the following procedure was found to be more convenient. A large volume of a solution of each salt was made up with a concentration equal to the

## MAP OF THE UNITED STATES

at 1000, and 10,000 feet of elevation. The dry divide is shown by oblique parallel lines, and the wet divide by horizontal lines of blue, and freshets by blue lines with

square dots in broken, rough points which have the effect of a surface on the map, are described, and of course not only the lines, but mountain summits. The line of the sea level, the datum, or zero level. The contour lines, layer, or the line that passes through the points of 1000 feet above this contour line, is the line, with a very slight variation of these contour lines indicates a gentle

descent, and the description of

the map.

to the 3000 feet, and  
quadrilateral areas are  
published in the same  
elevation, and latitude, as  
the Survey. The published  
areas are divided into  
fifteen localities, and  
the map.

on application.

The names of towns, cities, and towns in fact in 1860  
color, all letters, are  
printed. Boundaries,  
such as State, county, etc., and county lines, are  
colored, and the roads, lines of streams, roads  
and bridges. Roads are indicated by black blocks  
representing the face of the road, and  
crossed by small black lines. Roads are  
black, double lines, for the most roads, indi-  
cated for the interior of sections by single  
lines, and "abreast" lines, which cross with  
cross lines. Other colored  
crosses are represented by  
crossing roads.

The underwood.

The sheets comprising the topographic atlas are  
designated by letters, and a principal road, or  
the principal roads, or roads, which the letters  
and the names of sections, additional roads, are  
placed on the margin. The roads are colored  
for each road when fewer than 100 miles in  
length, but when they are greater in length  
the roads are colored.

was secured, by means of a copper wire, to the horizontal screen which protects the stirring paddles. The shaker was propelled by an independent motor placed on a shelf above the thermostat. The platform made one complete oscillation per second. By moving the propelling arm in or out in the slot in the wheel, the magnitude of the oscillation could be varied. The whole apparatus was made of brass, as was also a table for holding the stock solutions in the thermostat.

Drying Ovens and Furnace.- A Freas drying oven with automatic control, was used. The temperature was read on a thermometer inserted through an opening in the wall. A small Hoskins muffle furnace, which had been calibrated to an accuracy of perhaps  $5^{\circ}\text{C}$ , was used for drying the salts preparatory to making the standard solutions.

### 3. Method of Experimentation.-

(a) Solutions- The pure salts, dried as stated under the section headed "Materials", (pages 10 - 11) were weighed out in the calculated quantities for making a solution of the desired concentration. They were dissolved in water in a Jena beaker and the solution was then transferred quantitatively to a volumetric flask and diluted to the mark at  $25^{\circ}\text{C}$ . All of the flasks were calibrated at this temperature in the usual manner, by weighing into them the calculated amount of freshly distilled water and bringing them to  $25^{\circ}\text{C}$ . in the thermostat. The solutions were then transferred to bottles of "Resistenz" glass. Whenever a large number of determinations were to be made at the same total concentration, the following procedure was found to be more convenient. A large volume of a solution of each salt was made up with a concentration equal to the



total concentration of the mixed salt solution desired; then by mixing the two solutions in the proper proportions, solutions could be made in which the ratio of the salts varied, but which had a total concentration equal to that of each pure solution alone.

(b) Equilibrium.- Fifty cubic centimeters of the mixed salt solution were placed in the reaction flask and the whole balanced on a small trip balance. A quantity of sodium or potassium amalgam, sufficient to yield from 0.25 to 0.30 gram of alkali metal chlorides, was weighed into the flask from the sealing bottle. Since all of the amalgams contained approximately one milligram equivalent of alkali metal in ten grams, 60 grams was usually taken. The weight of the amalgam was not accurately determined, but it was probably known within 1.0% in each case. Where the concentration of the amalgam differed much from one milligram equivalent in ten grams, a correspondingly larger or smaller quantity was taken. The flasks were then placed in the thermostat and shaken for twenty minutes, after which the solutions were decanted from the amalgams and quickly replaced by a fresh portion. The stock solution was kept in the thermostat all of the time except while the change of solution was being made. The reaction flask was again placed on the shaking apparatus and agitated for twenty minutes. This process was repeated at least five times with 50 c.c. portions of solution if the total concentration of the solution was less than normal. For solutions that were normal or above, one 50 c.c. and three 25 c.c. portions were found to be sufficient to produce the desired equilibrium.

About eight minutes were required to change the solutions on the six amalgams held at one time upon the shaking apparatus. The shaking was not stopped during all of this time; however. The five flasks



left on the rack were agitated while the change of solution was being made on the sixth. Finally the amalgams were washed as described by G. McP. Smith. (6)

(c) Washing the Amalgams. - Five 150 c.c. beakers, each containing about 100 c.c. of distilled water, were placed in a row; the reaction flask was removed from the thermostat, the aqueous solution decanted and the amalgam poured into beaker number one. The water was then quickly decanted and the amalgam poured into beaker number two. After passing successively through all five beakers, the amalgam was placed in a 50 c.c. flask containing about 20 c.c. of very dilute HCl, where decomposition took place rapidly. The washing of the amalgam was complete in this way. In one case where a 0.60 normal solution of the chlorides was decanted from the reaction flask, the wash water from the third beaker gave no precipitate with silver nitrate. It took about <sup>one</sup> <sub>A</sub> minute from the time the amalgam was removed from the thermostat to wash it and get it into the decomposition flask.

That the action of the water upon the amalgam is negligible is shown by the following: An equivalent mixture of  $K_2SO_4$  and  $Na_2SO_4$ , at a total concentration of 0.20 normal, was decanted from the amalgams after twenty minutes agitation in the thermostat. 100 c.c. of this solution required only 1.66 c.c. of 0.10 normal HCl for its neutralization. (Methyl-orange) This corresponds to an alkalinity of 0.00166 normal. Furthermore, 60 grams of amalgam were allowed to stand over night in distilled water without complete decomposition.

(d) Drying of the Mixed Chlorides. - The HCl solution containing the alkali metals was drawn off from the mercury in the decomposi-



tion flask and evaporated to dryness in a weighed platinum or porcelain dish. At this point it is well to call attention to the fact that no attempt was made to remove the solution from the mercury quantitatively. As much as possible was removed with a pipette, but the mercury was not washed. It is the ratio between the alkali metals that is sought and not the total amount of each. Therefore, in the tables which will follow, the weight of "mixed chlorides" is only an approximate measure of the concentration of the metals in the amalgams.

The mixed chlorides were dried in the electric oven at  $160^{\circ}\text{C}$ . for at least two hours. It is recognized that this is not in accordance with the usual procedure. In most cases where sodium and potassium are to be separated, ammonium salts have to be gotten rid of, and the alkali metal chlorides must therefore be heated nearly to their fusion points. That drying at  $160^{\circ}\text{C}$ . is adequate for this work was shown by the following experiment: 0.1094 gram of fused NaCl and 0.2236 gram of fused KCl were dissolved in water in a weighed platinum dish, and about 1.0 c.c. of dilute HCl was added. This is about the ratio in which the salts occur in most of the amalgams at equilibrium. The solution was evaporated on the water bath and the residue dried at  $160^{\circ}\text{C}$ . for two hours. It contained 1.2 milligrams of water, and after twelve more hours in the oven at  $160^{\circ}\text{C}$ . it contained 1.0 milligram of water. In the calculations, since the sodium is gotten by difference, this retained water would all fall on the sodium. A recalculation of an actual experiment showed that where equilibrium was brought about with a solution containing five equivalents of potassium to one of sodium, the error due to this water would be about 1.0% of the actual value of  $C_c$ .



In cases where the equilibrium was brought about with equivalent mixtures of alkali salts, the error would be less than 0.50%. Since we were not able to check duplicate values of the equilibrium constant closer than 1.0%, when all analyses were made under the same conditions and would therefore be subject to constant errors of the same magnitude, it was not deemed necessary to dry the salts at the higher temperature. Drying at a higher temperature introduces the possibility of errors due to decrepitation.

(e, Separation of Sodium from Potassium.- The weighed mixed chlorides were dissolved in a small volume of water and about 0.50 cubic centimeter of chloro-platinic acid, in excess of the quantity required to convert the whole into chloro-platinic acid, on the assumption that it consisted entirely of sodium chloride, was added. The solution was evaporated on a slow water bath until the odor of HCl was not perceptible upon stirring the residue with a blunt glass rod. The dish was protected from direct contact with steam by a sheet of paper. If the solution gets too hot, hydrolysis will take place and the subsequent treatment with alcohol will leave a dark residue. Methyl alcohol (18) was then added and the residue thoroughly broken up with a glass rod. After allowing the residue to settle, the alcoholic solution of the sodium chloro-platinic acid was decanted through a filter paper that had been moistened with alcohol. The alcoholic solution of chloro-platinic acid has a great tendency to "creep". and for this reason the chloro-platinic method is often avoided by many analysts. Difficulties due to this were eliminated in the following way. The ends of three glass rods <sup>1</sup>were fused together in such a way that the rods made an angle of 120° but were not in the same plane. By placing them on a funnel,



the center fell below the rim. The dish was placed upon the rods and a small stream of alcohol, from the constricted end of a separatory funnel, was directed upon the edge of the dish in such a manner that most of the alcohol went inside of the dish while some went outside. That which went outside followed the rods to the center and then dripped into the paper filter. In this way the dish could be washed inside and out with very little alcohol and no danger of loss of precipitate. Washing of the  $K_2PtCl_6$  was continued in this manner until the alcohol was almost colorless. The dish was then placed under the funnel and any potassium salt that had gone onto the paper was washed back into the dish with boiling water. Ten or twelve drops of chloro-platinic acid, together with a few drops of HCl to prevent hydrolysis, were added and the solution evaporated. The residue was extracted with alcohol and washed by decantation until the alcohol came off colorless. Any potassium salt that had decanted onto the filter paper was washed back into the dish and the solution evaporated to dryness. By making the second evaporation with a few drops of chloro-platinic acid, the  $K_2PtCl_6$  finally obtained was always of a pure golden yellow color; otherwise it had the appearance of being contaminated with the sodium salt.

The  $K_2PtCl_6$  was dried in the oven at  $160^{\circ}C.$  for at least 45 minutes. Five samples dried in this way did not change in weight after two hours more at the same temperature. The weight of KCl was found by using the conversion factor of 0.3056. (See page 12.)



## IV. EXPERIMENTAL DATA..

The following tables contain the experimental data which has been obtained in this investigation. The figures in the first column refer to the number of the experiment; the second and third columns contain the normality of the potassium and sodium salts, respectively. The sum of these values gives the total normality of the solution. Columns four and five show the mol. fractions of  $\text{KHg}_m$  and  $\text{NaHg}_n$  in the amalgam at the start. Column six shows the weight of mixed  $\text{KCl}$  and  $\text{NaCl}$  which was gotten by the decomposition of the amalgam, after equilibrium had been established between it and the solution whose composition is represented in the second and third columns. The seventh column gives the weight of  $\text{K}_2\text{PtCl}_6$  which was obtained in the analysis of the "mixed chlorides". From the data contained in columns six and seven the mol fraction of  $\text{KHg}_m$  and  $\text{NaHg}_n$  in the amalgam at equilibrium may be calculated, and these are given in columns eight and nine. The last column shows the value of the expression,

$$\frac{(\text{KHg}_m) (\text{Na salt})}{(\text{NaHg}_n) (\text{K salt})} = C_c,$$

which is calculated from the data of the second, third, eighth and ninth columns.

There are three studies which can be made from these equilibria: first, the effect of varying the ratio in which the salts are mixed in solutions whose total concentration remains constant: second, the effect of varying the total concentration, but keeping the relative concentrations the same: third, the effect of changing the temperature. From the latter data the heat of the reaction may be calculated by means of the  $\text{Van't Hoff}$  equation.

TABLES I to IV ,inclusive, contain the data of the first class.



TABLE I.

KCl-NaCl

TOTAL CONCENTRATION 0.20

TEMPERATURE 25° C.

No.	Normal con- centration of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus KCL	Wt. K <sub>2</sub> PtCl <sub>6</sub>	Mol fract. in amalg. at equilib.		C <sub>C</sub>
	KCl	NaCl	KHg <sub>m</sub>	NaHg <sub>m</sub>			KHg <sub>m</sub>	NaHg <sub>m</sub>	
1.	.1600	.0400	.53	.47	.2888	.6197	.5990	.4010	.373
2.	.1600	.0400	.75	.25	.2840	.6173	.6080	.3920	.387
3.	.1333	.0666	.43	.57	.3195	.5165	.4336	.5664	.382
4.	.1333	.0666	.75	.25	.2792	.4502	.4324	.5676	.381
5.	.1000	.1000	1.0		.2550	.2722	.2752	.7248	.379
6.	.1000	.1000		1.0	.2700	.2902	.2771	.7229	.383
7.	.0666	.1333	.13	.87	.2804	.1829	.1633	.8367	.389
8.	.0666	.1333	.27	.73	.2970	.1907	.1607	.8393	.383
9.	.0400	.1600	1.0		.2585	.0910	.0939	.9061	.390
10.	.0400	.1600	.43	.57	.2366	.0837	.0868	.9132	.380
							Mean		.383

Na amalgam used contained 0.234% Na,  
K amalgam used contained 0.293% K.

Total wt. of amalgam used was about 60 grams.



TABLE II.

K<sub>2</sub>SO<sub>4</sub> - Na<sub>2</sub>SO<sub>4</sub>

No.	TOTAL CONCENTRATION 0.60 N.				TEMPERATURE 25° C.				° C
	Normal con- centration of salts.	Mol fract. in amalg. at start.	Wt. NaCl plus KCl.	Wt. K <sub>2</sub> PtCl <sub>6</sub>	Mol fract. in amalg. at equilib.	KHg <sub>m</sub>	NaHg <sub>m</sub>		
	K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	KHg <sub>m</sub>	NaHg <sub>m</sub>					
1.	.500	.100	.57	.43	.2687	.6259	.6593	.3407	.387
2.	.500	.100	.57	.43	.3161	.7376	.6612	.3388	.390
3.	.500	.100	1.0		.2776	.6469	.6599	.3401	.388
4.	.500	.100	1.0		.2775	.6494	.6632	.3368	.394
5.	.400	.200	.40	.60	.2368	.3905	.4434	.5566	.398
6.	.400	.200	.40	.60	.2400	.3918	.4384	.5616	.390
7.	.400	.200	1.0		.2488	.4050	.4370	.5630	.388
8.	.400	.200	1.0		.2775	.4481	.4330	.5670	.382
9.	.300	.300	.20	.80	.2434	.2650	.2811	.7189	.391
10.	.300	.300	.20	.80	.2867	.3093	.2784	.7216	.385
11.	.300	.300	1.0		.2595	.2772	.2753	.7247	.380
12.	.300	.300	1.0		.2555	.2727	.2752	.7248	.380
13.	.200	.400		1.0	.2397	.1594	.1666	.8333	.400
14.	.200	.400		1.0	.1722	.1115	.1620	.8380	.387
15.	.200	.400	1.0		.2563	.1632	.1594	.8406	.379
16.	.200	.400	1.0		.2795	.1778	.1589	.8411	.379
17.	.100	.500		1.0	.2185.	.0640	.0715	.9285	.385
18.	.100	.500		1.0	.2263	.0660	.0716	.9284	.385
19.	.100	.500	1.0		.2657	.0764	.0701	.9299	.378
20.	.100	.500	1.0		.2583	.0769	.0726	.9274	.392
							Mean		.387

Na amalgam used contained 0.157% Na.

K amalgam used contained 0.349% K

Total wt. of amalgam used was about 60 grams.



TABLE III.

K<sub>2</sub>SO<sub>4</sub> - NaCl

TOTAL CONCENTRATION 0.60 N.

TEMPERATURE 25° C.

No.	Normal con- centration of salts.		Mol. fract. in amalg. at start.		Wt. NaCl plus KCl.	Wt. K <sub>2</sub> PtCl <sub>6</sub>	Mol. fract., in amalg. at equilib.		C <sub>C</sub>
	K <sub>2</sub> SO <sub>4</sub>	NaCl	KHg <sub>m</sub>	NaHg <sub>n</sub>			KHg <sub>m</sub>	NaHg <sub>n</sub>	
1.	.500	.100		1.0	.2255	.5257	.6595	.3405	.388
2.	.500	.100		1.0	.2527	.5824	.6514	.3486	.374
3.	.500	.100	1.0		.2040	.4788	.6653	.3347	.397
4.	.500	.100	1.0		.2230	.5187	.6583	.3417	.385
5.	.500	.100	1.0		.2273	.5296	.6600	.3400	.388
6.	.400	.200		1.0	.1461	.2419	.4452	.5584	.401
7.	".400	.200		1.0	.2575	.4151	.4321	.5679	.380
8.	.400	.200	1.0		.2095	.3428	.4402	.5598	.393
9.	.400	.200	1.0		.1644	.2730	.4467	.5533	.404
10.	.300	.300		1.0	.2170	.2405	.2868	.7138	.401
11.	.300	.300		1.0	.1711	.1875	.2827	.7173	.394
12.	.300	.300	1.0		.1887	.2072	.2795	.7205	.388
13.	.300	.300	1.0		.2284	.2478	.2798	.7202	.389
14.	.300	.300		1.0	.2755	.2711	.2520	.7480	(.337)
15.	.300	.300	1.0		.2165	.2267	.2690	.7310	(.368)
16.	.200	.400		1.0	.2763	.1747	.1581	.8419	.376
17.	.200	.400		1.0	.2520	.1590	.1578	.8422	.376
18.	.200	.400	1.0		.1942	.1256	.1611	.8389	.384
19.	.200	.400	1.0		.2038	.1300	.1596	.8404	.380
20.	.100	.500		1.0	.2526	.0764	.0738	.9262	.399
21.	.100	.500		1.0	.2484	.0782	.0770	.9230	(.416)
22.	.100	.500	1.0		.2815	.0782	.0678	.9322	(.364)
23.	".100	.500		1.0	.2560	.0713	.0678	.9322	(.364)
							Mean	.388	

The Na amalgam contained 0.234% Na and 60 grams were used.  
 The K amalgam contained 0.386% K and 60 grams were used.



TABLE IV.

KCl-Na<sub>2</sub>SO<sub>4</sub>

TOTAL CONCENTRATION 0.60 N.					TEMPERATURE 25° C.				
No.	Normal con- centration of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus NaCl.	Wt. K <sub>2</sub> PtCl <sub>6</sub>	Mol fract. in amalg. at equilib.		C <sub>c</sub>
	KCl	Na <sub>2</sub> SO <sub>4</sub>	Kh <sub>gm</sub>	NaH <sub>gn</sub>			Kh <sub>gm</sub>	NaH <sub>gn</sub>	
1.	.500	.100	.50	.50	.2525	.5847	.6546	.3454	.379
2.	.500	.100	.25	.75	.2650	.6190	.6618	.3382	.391
3.	.500	.100	.63	.37	.3257	.7629	.6638	.3362	.395
4.	.500	.100	1.0		.2566	.5990	.6610	.3390	.390
5.	.400	.200	.25	.75	.3083	.5040	.4394	.5609	.391
6.	.400	.200	1.0		.3181	.5260	.4446	.5554	.400
7.	.400	.200	1.0		.2127	.3475	.4328	.5672	.381
8.	.400	.200	.50	.50	.1870#	.3058	.4390	.5610	.391
9.	.300	.300		1.0	.2320	.2485	.2762	.7238	.381
10.	.300	.300	1.0		.1635#	.1791	.2828	.7172	.394
11.	.300	.300	.25	.75	.2649	.2886	.2812	.7188	.391
12.	.300	.300	1.0		.3137	.3422	.2818	.7182	.392
13.	.200	.400	.85	.15	.2833	.1845	.1630	.8370	.390
14.	.200	.400	1.0		.2876	.1886	.1669	.8331	.400
15.	.200	.400		1.0	.2330	.1482	.1591	.8409	.379
16.	.200	.400	.50	.50	.2006	.1293	.1613	.8387	.384
17.	.100	.500	1.0		.1785#	.0533	.0728	.9272	.393
18.	.100	.500		1.0	.3206	.0918	.0698	.9302	.376
19.	.100	.500	1.0		.2931	.0873	.0729	.9271	.393
								Mean	.389
20.	.400	.200	.75	.25	.0858*	.1474	.4640	.5360	.433
21.	.300	.300	.25	.75	.1708#	.1972	.2990	.7010	.427
22.	.300	.300	.50	.50	.1672#	.1917	.2975	.7025	.423
23.	.100	.500		1.0	.2434	.0788	.0792	.9208	.430
24.	.100	.500	.50	.50	.2388	.0778	.0799	.9201	.434

one and Nos. 20-24 were run at the same time. Upon repeating the determinations the values given in the main table were obtained.

\* This amalgam evolved hydrogen quite vigorously.

# Slight evolution of hydrogen.

The Na amalgam contained 0.157% of Na and 75 grams were used.

The K amalgam contained 0.296% of K and 75 grams were used.



In TABLE I, page 25, will be found the data for sodium and potassium chlorides in varying ratios, with a total concentration of 0.20 N. An examination of the last column shows very conclusively that under the conditions, the equilibrium is in accordance with the mass law expression even over widely varying ratios.

TABLE II, page 26, contains similar data for mixtures of  $K_2SO_4$  and  $Na_2SO_4$  at a total concentration of 0.60 normal. In this series, the higher total concentration made it possible to vary the ratios between still wider limits than was feasible in TABLE I. Here again the value of  $C_c$  remains constant over the range studied.

In TABLES III and IV, pages 27 and 28, the same holds true, even though in these cases we have salts of two different types and with no common ion. It is interesting to note that the values of the constants obtained for each of the mixtures are practically identical; the mean values range from .383 to .389. In view of the fact that additional data for more concentrated solutions will be given in the latter part of this paper, it seems advisable to postpone the discussion of this case.

TABLE V, page 30, contains the results of an attempt to study the effect of changing the total concentration of the mixed salts, keeping the relative concentrations the same. The results are far from satisfactory. In the first seven experiments of TABLE V, where the solutions and the amalgams used were identical, the value of  $C_c$  varied from .348 to .417. Such a variation could not possibly have been due to analytical error. So far as could be ascertained, there was no reason whatever to believe that any of the analyses were wrong. All of the precipitates were of a pure golden yellow and the analysis appeared normal throughout. It will be noted that the



TABLE V.

30.

 $K_2SO_4$  -  $Na_2SO_4$ 

TOTAL CONCENTRATION 0.20 to 2.00 N.

TEMPERATURE 25° C.

No.	Normal con- centration of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus KCl	Wt. $K_2PtCl_6$	Mol fract. in amalg. at equilib.		C c
	$K_2SO_4$	$Na_2SO_4$	$KHg_m$	$NaHg_m$			$KHg_m$	$NaHg_m$	
1.	0.10	0.10	.25	.75	.1800*	.1963	.2818	.7182	.392
2.	0.10	0.10	.25	.75	.1916*	.2168	.2945	.7055	.417
3.	0.10	0.10	.25	.75	.3582	.3528	.2608	.7392	.353
4.	0.10	0.10	1.00		.2222	.2406	.2792	.7208	.388
5.	0.10	0.10	1.00		.3514	.3606	.2638	.7362	.358
6.	0.10	0.10	.25	.75	.3673	.3694	.2581	.7410	.348
7.	0.10	0.10	1.00		.3546	.3610	.2615	.7385	.354
8.	0.25	0.25	.80	.20	.2009*	.2170	.2798	.7202	.389
9.	0.25	0.25	.80	.20	.3912	.3919	.2570	.7430	.346
10.	0.25	0.25	1.00		.2828	.2981	.2714	.7286	.373
11.	0.25	0.25	1.00		.3409	.3496	.2635	.7365	.358
12.	0.25	0.25	1.00		.2597	.2682	.2658	.7342	.362
13.	0.25	0.25	1.00		.3654	.3688	.2592	.7408	.350
14.	0.50	0.50	.20	.80	.2028*	.2191	.2787	.7213	.381
15.	0.50	0.50	.20	.80	.2047*	.2238	.2821	.7179	.393
16.	0.50	0.50	.20	.80	.3596	.3600	.2569	.7431	.346
17.	0.50	0.50	1.00		.2828	.2981	.2714	.7286	.373
18.	0.50	0.50	1.00		.3771	.3660	.2302	.7698	.329
19.	0.50	0.50	1.00		.3393	.3385	.2559	.7441	.344
20.	1.00	1.00	.20	.80	.3497	.3580	.2629	.7373	.357
21.	1.00	1.00	.20	.80	.3470	.3531	.2613	.7387	.354
22.	1.00	1.00	.20	.80	.3673	.3694	.2581	.7419	.348
23.	1.00	1.00	.20	.80	.3546	.3610	.2615	.7385	.354
24.	1.00	1.00	1.00		.2703	.2880	.2745	.7255	.378
25.	1.00	1.00	1.00		.2795	.2987	.2756	.7244	.380

Na amalgam used in each case contained 0.272% Na.

K amalgam used in each case contained 0.355% K.

The total amount of amalgam used was 60 grams

\* Hydrogen was evolved freely at first but the action finally ceased.



weight of mixed chlorides was much larger than in previous cases, this being due to the fact that the amalgams used were more concentrated than heretofore. The sodium amalgam contained 0.272% of Na and the potassium amalgam 0.355% of K. In experiments 1 and 2, hydrogen was evolved freely at first but this finally ceased almost entirely. This was a rather common phenomenon and is attributed to the catalytic action of dust particles which finally become disengaged. Impurities of heavy metals in the salts hasten the decomposition of the amalgams (see page 10) but in that case the reaction does not cease until the whole of the amalgam has been decomposed. By studying the mixed chloride column in connection with the value of  $C_c$  in the first seven experiments, it will be noted that the latter decreases with increasing weight of mixed chlorides. As has already been pointed out, (page 21) the weight of mixed chlorides does not give an exact measure of the of the weight of alkali metals in the amalgams; but it does represent it very closely. At least the relative amounts in two separate analyses can be judged by a comparison of these values. I have calculated the approximate percentages of sodium and potassium in the amalgams, from the weight of the mixed chlorides and of  $K_2PtCl_6$ . The values represent the minimum percentage concentrations <sup>at equilibrium</sup> and they are certainly very nearly correct. They are given in TABLE VI.

TABLE VI.

No.	Approximate percent of K.	$C_c$	No.	Approximate percent of Na.	$C_c$
1.	0.052%	.392	1.	0.078%	.392
2.	0.058	.417	2.	0.082	.417
4.	0.064	.388	4.	0.097	.388
3.	0.094	.353	5.	0.158	.378
5.	0.096	.358	7.	0.160	.354
7.	0.096	.354	3.	0.164	.353
6.	0.098	.348	6.	0.165	.348



The figures in the column headed "No" refer to the number of the experiment in TABLE V, page 30. From TABLE VI, it is evident that  $C_c$  is in some way dependent upon the concentration of the amalgams; a fact that had not been observed before, either by G. McP. Smith or the writer. If the results within any one of the four sets of data compiled in TABLE V are studied, the same will be found to be true.

A potassium amalgam that had stood in a sealed bottle for three years, and which had a thick layer of crystals on the surface, was analyzed by pouring the liquid through the capillary tube of the sealing bottle into standard HCl and titrating the excess of acid with sodium carbonate, using methyl orange as an indicator. The mean of two results showed that the amalgam contained only 0.0965% of potassium. This was peculiar in view of the fact that the literature is very concordant on the concentration of saturated potassium amalgams. (19)(20)(21). Kerp and Bottger found 0.47% K at  $20^{\circ}\text{C}$ . and 0.53% at  $25^{\circ}\text{C}$ . , while Smith and Bennett found 0.46% at  $20^{\circ}\text{C}$ . (The values 0.47 and 0.46 which appear in the rubidium column in their paper should be in the potassium column.)

The amalgam referred to above was then analyzed by G. McP. Smith, who decomposed it with HCl and weighed the KCl; he found the liquid to contain 0.0963% of potassium. Each of us converted the chloride into the chloro-platinate. 0.0797 gram of the chloride gave 0.2588 gram of the chloro-platinate; an amount which is equivalent to 0.0790 gram of KCl. The salt gave a characteristic potassium flame, and the agreement above is close enough to establish the fact that the bottle was not mislabeled. This leads us to conclude that  $\text{KHg}_m$  dissolves in mercury to form supersaturated solutions and that the true solubility is at least as low as 0.0963% of potassium. It is not certain whether this represents the true



equilibrium point or not, but it probably does. However, this same amalgam was analyzed several months later and was found to contain 0.0937% of potassium. This decrease is undoubtedly due, at least in part, to the oxidation of potassium by the air which was introduced at the time the first samples were withdrawn. The crystals adhered to the walls of the bottle and there was an air space between them and the liquid.

A sodium amalgam which had been kept in a sealed bottle for six years and two months was analyzed and found to contain 0.204% of sodium, but a careful examination showed that no crystals were present, so no final conclusion can be drawn as to the solubility of  $\text{NaHg}_m$ . It is, however, not likely that the amalgam had remained saturated during this long period. The solubility of the alkali and alkali-earth amalgams in mercury will be investigated in this laboratory at once. The fact that the solubility of potassium has been found to <sup>be</sup> about one-fifth of the previously published values makes it seem worth while to reinvestigate all of the solubility data.

In TABLE VI, it will be noted that when the percent of potassium equals 0.09, a very decided lowering effect is produced upon the value of  $C_c$ . This cannot be attributed to a separation of solid  $\text{KHg}_m$ , for that would cause  $C_c$  to increase, since  $\text{KHg}_m$  appears in the numerator of the mass law expression. It might be accounted for by the separation of  $\text{NaHg}_n$ , concerning the solubility of which we are at present very uncertain, but there is no evidence that this took place. If the amalgam is in a metastable condition, there is no way of predicting what its action may be; any effect might be produced by this cause.

When it became known that the concentration of the amalgams was a matter to be considered, a series of determinations was carried



out in which the original amalgams were diluted with varying amounts of mercury and then brought to equilibrium with an equivalent mixture of sodium and potassium chlorides whose total concentration was 0.20 normal. Unless otherwise stated, all work was done at 25° C. This study appears in TABLE VII., page 35. Column one contains numbers for reference; columns two and three, the number of grams of the respective amalgams used. Column four shows the weight of pure mercury that was added to the amalgam; columns five and six show, respectively, the weights of mixed chlorides which were obtained from the decomposition of the amalgam, and the weights of  $K_2PtCl_6$  which they yielded. In the seventh and eighth columns are given the number of milligram equivalents, times  $10^2$ , of potassium and of sodium per gram of mercury in the equilibrium mixture. The total weight of mercury is assumed to equal the sum of the weights of pure mercury and amalgams. Columns nine and ten show the percentages of alkali metals contained in the amalgams at equilibrium. The value of  $C_c$  is given in the last column.

Throughout the series, the concentration of the amalgam is gradually decreased until it reaches a value about one-fifth that of the original. With increasing dilution there is an increase in the value of  $C_c$ , and then a decrease. The maximum value is obtained by diluting 60 grams of the amalgam with 100 grams of pure mercury. Further dilution causes a slight decrease, but this does not exceed about 2.5%, on the average, and some of the values gotten by dilution with 150 grams of mercury are higher than some of the lowest gotten by dilution with 100 grams. Since the effect of further dilution was very slight, it was decided to make all future determinations by adding 100 grams of pure mercury to 60 grams of the amalgam. The results which have been obtained seem to fully justify this pro-



TABLE VII.

## KCl-NaCl

Showing the effect of diluting the amalgams with pure mercury.  
 The aqueous solution used was an equivalent mixture of KCl and NaCl.  
 Total concentration 0.20N. Temperature 25° C.

No.	Grams of amalgam used.		Grams of Hg added	Wt. KCl plus NaCl	Wt. $K_2PtCl_6$	Milligram equivalents per gm. of Hg at $\frac{1}{2}$ equilib. $\times 10^3$	Percent of alk. metals at equilibrium.		$C_c$	
	K	Na					K	Na		
1.	19	41*	none	.3669	.3777	2.58	7.25	.101	.167	.355
2.	19	41*	" "	.3716	.3800	2.60	7.26	.102	.167	.356
3.	19	41*	" "	.3620	.3706	2.53	7.10	.100	.163	.357
4.	22	38*	" "	.3395	.3529	2.41	6.60	.095	.151	.365
5.	22	38*	" "	.3451	.3546	2.42	6.75	.095	.155	.359
6.	22	38*	" "	.3475	.3581	2.45	6.80	.096	.156	.360
7.	18	42	" "	.2184	.2399	1.64	4.14	.065	.095	.396
8.	22	38	" "	.2567	.2796	1.91	4.90	.075	.112	.391
9.	--	60	100	.2504	.2963	.76	1.71	.029	.039	.444
10.	--	60	100	.2601	.3086	.79	1.77	.031	.041	.446
11.	--	60	100	.2638	.3076	.79	1.82	.031	.042	.433
12.	--	60	100	.2589	.3030	.78	1.78	.030	.041	.437
13.	60	--	100	.2977	.3514	.90	2.03	.035	.047	.442
14.	60	--	100	.2781	.3298	.84	1.90	.033	.043	.445
15.	60	--	100	.2399	.2830	.73	1.64	.028	.038	.442
16.	--	60	150	.2474	.2860	.56	1.30	.022	.030	.428
17.	--	60	150	.2740	.3133	.61	1.41	.023	.033	.421
18.	--	60	150	.2447	.2802	.55	1.30	.021	.030	.422
19.	60	--	150	.2687	.3089	.60	1.42	.023	.032	.425
20.	60	--	150	.2380	.2796	.55	1.24	.021	.029	.439
21.	60	--	150	.2354	.2768	.54	1.23	.021	.028	.440
22.	--	60	200	.2376	.2710	.43	1.02	.017	.023	.420
23.	60	--	200	.2658	.3046	.48	1.13	.019	.026	.422

\*The Na amalgam used here contained 0.272% Na. In all other cases the Na amalgam contained 0.191% Na. The K amalgam used contained 0.355% K.

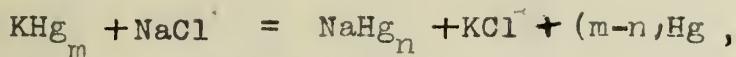


cedure. At this dilution no trouble was experienced in duplicating results, even though the concentrations of the amalgams at equilibrium often varied considerably, owing to a temporary evolution of hydrogen in some cases. When the undiluted amalgams were used, there was very often difficulty in getting check results. On looking over some of the earlier data, which does not appear in this paper, it is found that some of the inconsistent results can be explained from the standpoint of concentration, while some of them cannot. This tends to show that the behavior of the amalgams, when supersaturated, depends upon the condition of the amalgam at the time it is used. In the diluted amalgams the behavior is more dependable, as is evidenced by the fact that out of 144 determinations that were made under these conditions, only seven had to be thrown out for unknown causes. Six of these were made at one time with the same solution and they agreed among themselves, so it is almost certain that an error was made in preparing the solution. This is given merely as evidence to justify the addition of 100 grams of mercury. A more extended study of the effect of dilution will be made, with a view of determining its cause.



## HEAT OF REACTION.

G. McP. Smith (1) has made determinations of the equilibrium constant at 18°C. and at 24°C. The data which he obtained cannot be used to calculate the heat of the reaction because the solutions used at the two different temperatures were not identical. He finds that the reaction,



is endothermic. If the solutions used at the different temperatures are identical, and if the temperature range is not too large, the heat of reaction may be calculated from the equilibrium constants by means of the Van't Hoff equation,

$$2.303 \log_{10} \frac{C_2}{C_1} = \frac{\Delta U}{R} \cdot \left[ \frac{1}{T_1} - \frac{1}{T_2} \right],$$

where  $C_1$  and  $C_2$  are the values of the equilibrium constants at the absolute temperatures  $T_1$  and  $T_2$ , respectively:  $R$  is the gas constant expressed in calories and has the value 1.9852;  $\Delta U$  is the heat evolved when the substances in the numerator of the mass law expression react to form the substances in the denominator; i.e., when the above reaction proceeds from left to right.

The equilibrium constant has been determined at four different temperatures and the data are given in TABLES VIII to XI inclusive, pages 38 and 39. Sixty grams of amalgam were diluted with 100 grams of pure mercury and the aqueous solution used was an equivalent mixture of sodium and potassium chlorides at a total concentration of 0.20 normal. The mean values of the equilibrium constants are as follows:

Temperature.	$C_C$
15°	.520
20°	.473
25°	.440
30°	.397



TABLE VIII.

KCl-NaCl

TOTAL NORMALITY 0.200

TEMPERATURE 15°C.

No.	Normal con- centration of salts.			Mol fract. in amalg. at start.	Wt. NaCl plus KCl.	Wt. $K_2PtCl_6$	Mol fract. in amalg. at equilib.	$C_c$
	KCl	NaCl	$KHg_m$	$NaHg_n$			$KHg_m$	$NaHg_n$
1.	.100	.100		1.00*	.1600	.2113	.3425	.6575
2.	.100	.100		1.00	.3014	.3924	.3413	.6587
3.	.100	.100		1.00	.2957	.3854	.3417	.6583
4.	.100	.100		1.00	.2798	.3672	.3443	.6557
5.	.100	.100	1.00*		.1877	.2439	.3405	.6595
6.	.100	.100	1.00		.2844	.3729	.3430	.6560
7.	.100	.100	1.00		.3002	.3922	.3425	.6575
8.	.100	.100	1.00		.3045	.3940	.3391	.6609
							Mean	.520

Na amalgam used contained 0.191% Na. 60 grams used.

K amalgam used contained 0.355% K. 60 grams used.

\* 60 grams of mercury was added in Nos. 1 and 5.  
In all other cases 100 grams was added.

TABLE IX.

KCl-NaCl

TOTAL NORMALITY 0.200

TEMPERATURE 20°C.

No.	Normal con- centration of salts.			Mol fract. in amalg. at start.	Wt. NaCl plus KCl.	Wt. $K_2PtCl_6$	Mol fract. in amalg. at equilib.	$C_c$
	KCl	NaCl	$KHg_m$	$NaHg_n$			$KHg_m$	$NaHg_n$
1.	.100	.100		1.00	.2595	.3188	.3204	.6796
2.	.100	.100		1.00	.2882	.3550	.3214	.6786
3.	.100	.100		1.00	.2798	.3449	.3214	.6786
4.	.100	.100	1.00		.2833	.3472	.3195	.6805
5.	.100	.100	1.00		.2894	.3569	.3217	.6783
6.	.100	.100	1.00		.3073	.3805	.3231	.6769
							Mean	.477
								.473

Na amalgam used contained 0.191% Na. 60 grams used.

K amalgam used contained 0.355% K. 60 grams used.

100 grams of mercury was added in each case.



TABLE X.

KCl-NaCl

TOTAL NORMALITY 0.200

TEMPERATURE 25° C.

No.	Normal con- centration of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus KCl.	Wt. $K_2PtCl_6$	Mol fract. in amalg. at equilib.		"C" $c$
	KCl	NaCl	$KHg_m$	$NaHg_n$			$KHg_m$	$NaHg_n$	
1.	.100	.100		1.0	.2504	.2963	.3073	.6926	.444
2.	.100	.100		1.0	.2601	.3086	.3084	.6916	.446
3.	.100	.100		1.0	.2464	.2919	.3077	.6923	.444
4.	.100	.100		1.0	.2271	.2655	.3034	.6966	.436
5.	.100	.100		1.0	.2638	.3076	.3026	.6974	.433
6.	.100	.100		1.0	.2589	.3030	.3040	.6960	.437
7.	.100	.100	1.0		.2380	.2796	.3050	.6950	.439
8.	.100	.100	1.0		.2354	.2768	.3054	.6946	.440
9.	.100	.100	1.0		.2399	.2830	.3065	.6935	.442
10.	.100	.100	1.0*		.1737	.2083	.3120	.6880	(.454)
11.	.100	.100	1.0		.2977	.3514	.3067	.6933	.442
12.	.100	.100	1.0		.2781	.3298	.3082	.6918	.445
							Mean		.440

Na amalgam used contained 0.191% Na. 60 grams used.

K amalgam used contained 0.355% K. 60 grams used.

100 grams of mercury was added in each case.

\*This amalgam was the last of a bottle that had stood for several weeks. The air in the bottle had oxidized the K. Hence the low weight of mixed salts.

TABLE XI.

KCl-NaCl

TOTAL NORMALITY 0.200

TEMPERATURE 30° C.

No.	Normal con- centration of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus KCl.	Wt. $K_2PtCl_6$	Mol fract. in amalg. At equilib.		"C" $c$
	KCl	NaCl	$KHg_m$	$NaHg_n$			$KHg_m$	$NaHg_n$	
1.	.100	.100		1.0	.2551	.2773	.2807	.7193	.390
2.	.100	.100		1.0	.2766	.3036	.2835	.7165	.396
3.	.100	.100		1.0	.2432	.2685	.2853	.7147	.399
4.	.100	.100	1.0		.2651	.2914	.2838	.7162	.396
5.	.100	.100	1.0		.2855	.3157	.2859	.7141	.400
6.	.100	.100	1.0		.2811	.3109	.2858	.7142	.400
							Mean		,397

The amalgams used were the same as in the table above and 100 grams of mercury was added.



By substituting these values in the Van't Hoff equation and solving for  $\Delta U$ , it is found to equal -3180 calories between  $15^\circ$  and  $20^\circ$ ; -2560 calories between  $20^\circ$  and  $25^\circ$  and -3670 between  $25^\circ$  and  $30^\circ$  C. The mean of these values is -3140 calories. The results are not as concordant as might be desired; however, closely agreeing results are not to be expected, because of the fact that the magnitude of  $\log_{10} \frac{C_2}{C_1}$  changes 10% with a change of 1.0% in the numerical value of the fraction. In case each of the two values of  $C_2$  were in error by as much as 1.0%, and if the errors happened to be in opposite directions, the error made in computing the heat of the reaction would be 20%. All that can be said is that the heat of the reaction is in the neighborhood of -3000 calories between  $15^\circ$  and  $30^\circ$  C.

Berthelot (22) has made the only study of the heats of formation of liquid amalgams, but unfortunately, the least concentrated amalgam which he used contained 0.32% of potassium, and the sodium amalgam contained 0.45% of Na. The potassium amalgam which was used in this work contained, after dilution, approximately 0.13% of K. It is not possible, therefore, to calculate the heat of the reaction from any existing data. A calculation, using the <sup>data</sup> <sub>from</sub> Berthelot's most dilute amalgams, together with the necessary data from Landolt and Börnstein, showed the heat of reaction to be -6400 calories. In view of the fact that the difference in the concentrations of the amalgams is great, a comparison is meaningless, except to show the order. Even though 0.32% potassium amalgam were used, Berthelot's data could not be used with accuracy because it does not include the heat of formation of a sodium amalgam which in concentration is equivalent to the potassium amalgam. Therefore the -6400 calor-



41.

ies is only a very rough approximation, when it is considered in the light of our conditions.

#### THE EFFECT OF INCREASING THE TOTAL CONCEN-- CENTRATION OF THE SALT SOLUTION.

##### 1. Salts with a Common Ion.

(a) KCl-NaCl.- G.McP.Smith (1) studied the effect of increasing the total concentration of mixed sodium and potassium chlorides, in which the salts are present in equivalent quantities. He found, that by increasing the concentration from 0.20 normal to 2.0 normal, the value of the equilibrium constant,  $C_c$ , decreased from 0.472 to 0.395, at 18°C. Upon calculating the ion fractions of the sodium and potassium by means of the equations,

$$(K^+) = \frac{(KHg_m)}{(KHg_m) + (NaHg_n) C_0} \quad \text{and} \quad (Na^+) = 1 - (K^+)$$

(see page 8), it was found that "The concentration of the  $Na^+$  ion gains on that of the potassium ion", with increasing total salt concentration. G.McP.Smith's experiments were carried out with 0.26% sodium and 0.33% potassium amalgams. Since it has been found that potassium amalgams at concentrations greater than 0.096% contain potassium in a metastable condition, it has seemed advisable to repeat the work with more dilute amalgams. This has been done at 25°C., using equivalent mixtures of sodium and potassium chlorides. The data will be found in Table XII, page 42.

Experiments 14 to 28, inclusive, were carried out with solutions in which the salts were present in proportions other than equivalent, and they will be discussed later. The total concentration of the equivalent mixtures was increased from 0.20 normal to 4.0 normal and the value of  $C_c$  was found to decrease from .440 to .322. The

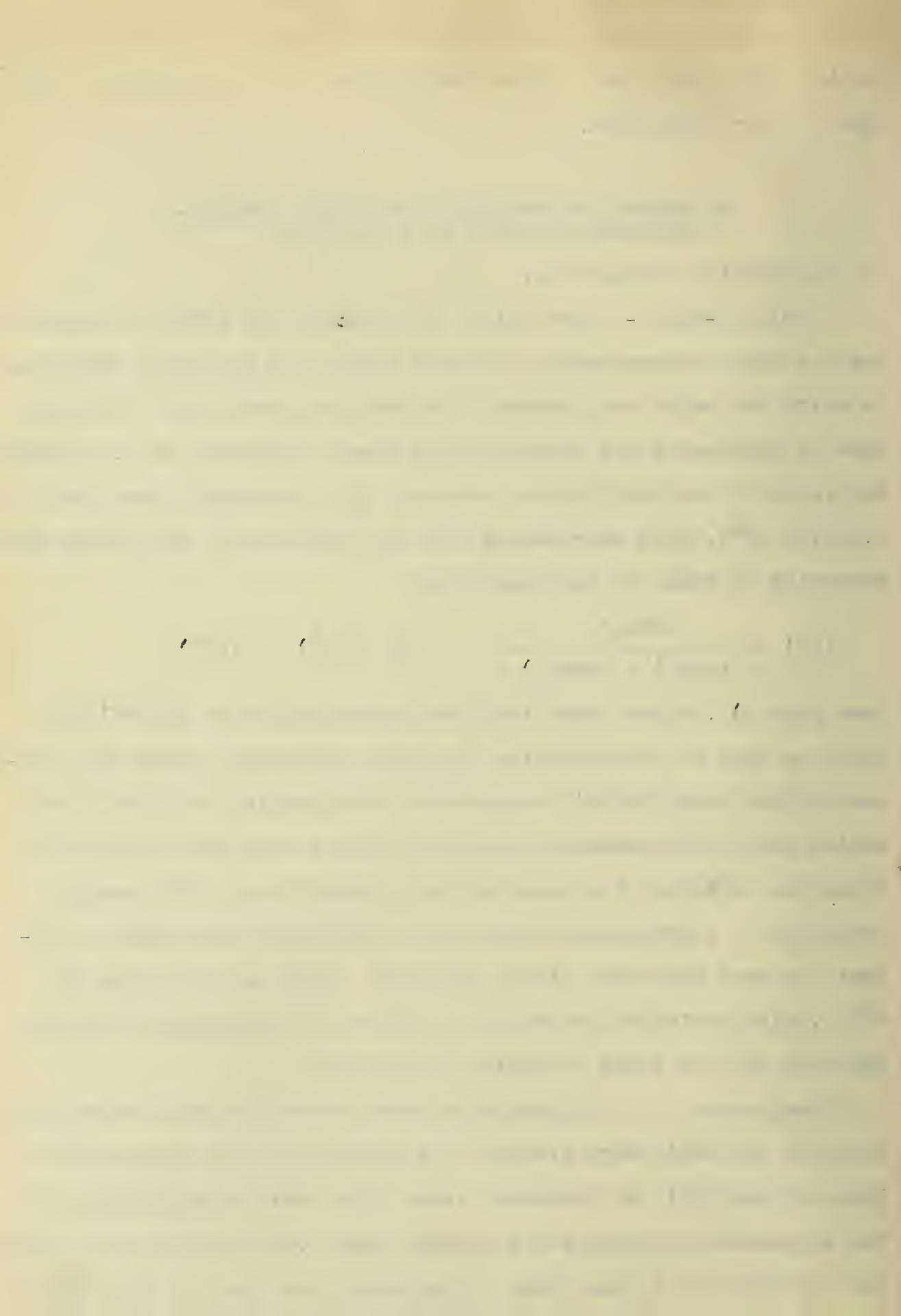


TABLE XII.

### KCl - NaCl

TOTAL CONCENTRATION 0.20 N. to 4.0 N,

TEMPERATURE 25° C.

No.	Normal concentration of salts.		Mol fract. in amalg. at start.		Wt. NaCl plus KCl.	Wt. K <sub>2</sub> PtCl <sub>6</sub>	Mol fract. in amalg. at equilib.		C,
	KCl	NaCl	KHg <sub>m</sub>	NaHg <sub>n</sub>			KHg <sub>m</sub>	NaHg <sub>n</sub>	
1.	0.10	0.10							Mean .440
2.	0.25	0.25		1.0	.2649	.3080	.3019	.6981	.432
3.	0.25	0.25		1.0	.2698	.3129	.3009	.6991	.430
4.	0.25	0.25	1.0		.2366	.2768	.3038	.6962	.436
5.	0.25	0.25	1.0		.2616	.3064	.3042	.6958	.437
								Mean ,434	
6.	0.50	0.50		1.0	.2848	.3253	.2959	.7041	.421
7.	0.500	0.50		1.0	.2957	.3379	.2962	.7038	.421
8.	0.50	0.50	1.0		.2591	.2955	.2953	.7047	.419
9.	0.50	0.50	1.0		.3087	.3490	.2927	.7073	.414
								Mean ,419	
10.	1.0	1.0		1.0	.3204	.3427	.2757	.7243	.381
11.	1.0	1.0		1.0	.3195	.3444	.2781	.7219	.385
12.	1.0	1.0	1.0		.3075	.3290	.2757	.7243	.381
13.	1.00	1.0	1.0		.2845	.3024	.2740	.7260	.377
								Mean ,381	
14.	1.66	0.33	.62	.38	.3764	.8678	.6515	.3448	.374
15.	1.66	0.33	.62	.38	.3791	.8793	.6561	.3439	.382
16.	1.66	0.33	1.0		.3291	.7607	.6536	.3464	.377
17.	1.66	0.33	1.0		.3313	.7652	.6532	.3468	.377
18.	1.66	0.33		1.0	.3294	.7688	.6612	.3388	.390
19.	1.66	0.33		1.0	.3473	.8119	.6623	.3377	.392
20.	1.66	0.33	1.0		.3694	.8630	.6614	.3386	.391
21.	1.66	0.33	.33	.67	.3660	.8275	.6368	.3632	(.351)
								Mean ,383	
22.	0.33	1.66		1.0	.2607	.0750	.0689	.9311	.371
23.	0.33	1.66		1.0	.2853	.0808	.0692	.9308	.372
24.	0.33	1.66		1.0	.2739	.0779	.0694	.9306	.373
25.	0.33	1.66	1.0		.2161	.0628	.0708	.9292	.382
26.	0.33	1.66	1.0		.2194	.0626	.0695	.9305	.374
27.	0.33	1.66	1.0		.2126	.0616	.0706	.9294	.381
28.	0.33	1.66	1.0		.2727	.0789	.0705	.9295	.381
								Mean ,376	
29.	2.00	2.00		1.0	.3018	.2886	.2446	.7554	.324
30.	2.00	2.00		1.0	.3088	.2919	.2424	.7576	.320
31.	2.00	2.00	1.0		.2985	.2832	.2424	.7576	.320
32.	2.00	2.00	1.0		.2971	.2856	.2460	.7540	.326
								Mean ,322	



TABLE XIII.

K<sub>2</sub>SO<sub>4</sub> - Na<sub>2</sub>SO<sub>4</sub>

TOTAL CONCENTRATION 0.20 to 2.0 N.

TEMPERATURE 25°C.

No.	Normal concentration of salts.		Mol fract. in amalg., at start.	Wt. NaCl plus KCl.	Wt. K <sub>2</sub> PtCl <sub>6</sub>	Mol fract. in amalg. at equilib.	K <sub>2</sub> Hg <sub>n</sub>	NaHg <sub>n</sub>	C <sub>c</sub>
	K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	KHg <sub>n</sub>			NaHg <sub>n</sub>			
1.	0.10	0.10		1.0	.2439	.2831	.3010	.6990	.431
2.	0.10	0.10		1.0	.2923	.3379	.2999	.7001	.428
3.	0.10	0.10		1.0	.2816	.3257	.3000	.7000	.428
4.	0.10	0.10		1.0	.2939	.3394	.2996	.7004	.428
5.	0.10	0.10	1.0		.2811	.3318	.3067	.6933	.442
6.	0.10	0.10	1.0		.2822	.3305	.3041	.6959	.437
7.	0.10	0.10	1.0		.2600	.3073	.3073	.6927	.443
8.	0.10	0.10	1.0		.2354	.2746	.3026	.6974	.434
								Mean	.434
9.	0.50	0.50		1.0	.2828	.3280	.3010	.6990	.431
10.	0.50	0.50		1.0	.2810	.3281	.3030	.6970	.435
11.	0.50	0.50		1.0	.2999	.3496	.3025	.6975	.434
12.	0.50	0.50		1.0	.3223	.3743	.3013	.6987	.431
13.	0.50	0.50	1.0		.2800	.3264	.3029	.6971	.434
14.	0.50	0.50	1.0		.2810	.3275	.3024	.6976	.434
15.	0.50	0.50	1.0		.2907	.3372	.2983	.7017	.425
16.	0.50	0.50	1.0		.2616	.3040	.3016	.6984	.432
								Mean	.432
17.	0.833	0.166		1.0	.3246	.7814	.6858	.3142	.436
18.	0.833	0.166		1.0	.3833	.9221	.6836	.3164	.432
19.	0.833	0.166		1.0	.3670	.8811	.6854	.3146	.435
20.	0.833	0.166	1.0		.3107	.7476	.6854	.3146	.435
21.	0.833	0.166	1.0		.2940	.7086	.6866	.3134	.438
22.	0.833	0.166	1.0		.3155	.7572	.6840	.3160	.431
								Mean	.434
23.	0.166	0.833		1.0	.2920	.0927	.0778	.9222	.421
24.	0.166	0.833		1.0	.3004	.0958	.0781	.9219	.423
25.	0.166	0.833		1.0	.2825	.0896	.0776	.9224	.420
26.	0.166	0.833		1.0	.3160	.1003	.0780	.9220	.422
27.	0.166	0.833	1.0		.2626	.0858	.0788	.9212	.427
28.	0.166	0.833	1.0		.2913	.0944	.0800	.9200	.431
29.	0.166	0.833	1.0		.2740	.0862	.0769	.9231	.417
30.	0.166	0.833	1.0		.2872	.0908	.0773	.9227	.419
								Mean	.423
31.	1.0	1.0		1.0	.3400	.3895	.2968	.7032	.422
32.	1.0	1.0		1.0	.2822	.3266	.3001	.6999	.429
33.	1.0	1.0		1.0	.3071	.3558	.3005	.6995	.429
34.	1.0	1.0		1.0	.3270	.3766	.2988	.7012	.426
35.	1.0	1.0	1.0		.3040	.3534	.3018	.6982	.432
36.	1.0	1.0	1.0		.2938	.3409	.3010	.6990	.431
37.	1.0	1.0	1.0		.2481	.2885	.3017	.6983	.432
38.	1.0	1.0	1.0		.3031	.3516	.3010	.6990	.430
								Mean	.429

Na amalgam used contained 0.288% Na. K amalgam was 0.328% K.

Used 46 grams Na amalgam with 120 gms. of Hg.

Used 60 grams K amalgam with 100 gms. of Hg.



TABLE XIV.

KCl-Na<sub>2</sub>SO<sub>4</sub>

TOTAL CONCENTRATION 0.20 to 3.0N.

TEMPERATURE 25 C.

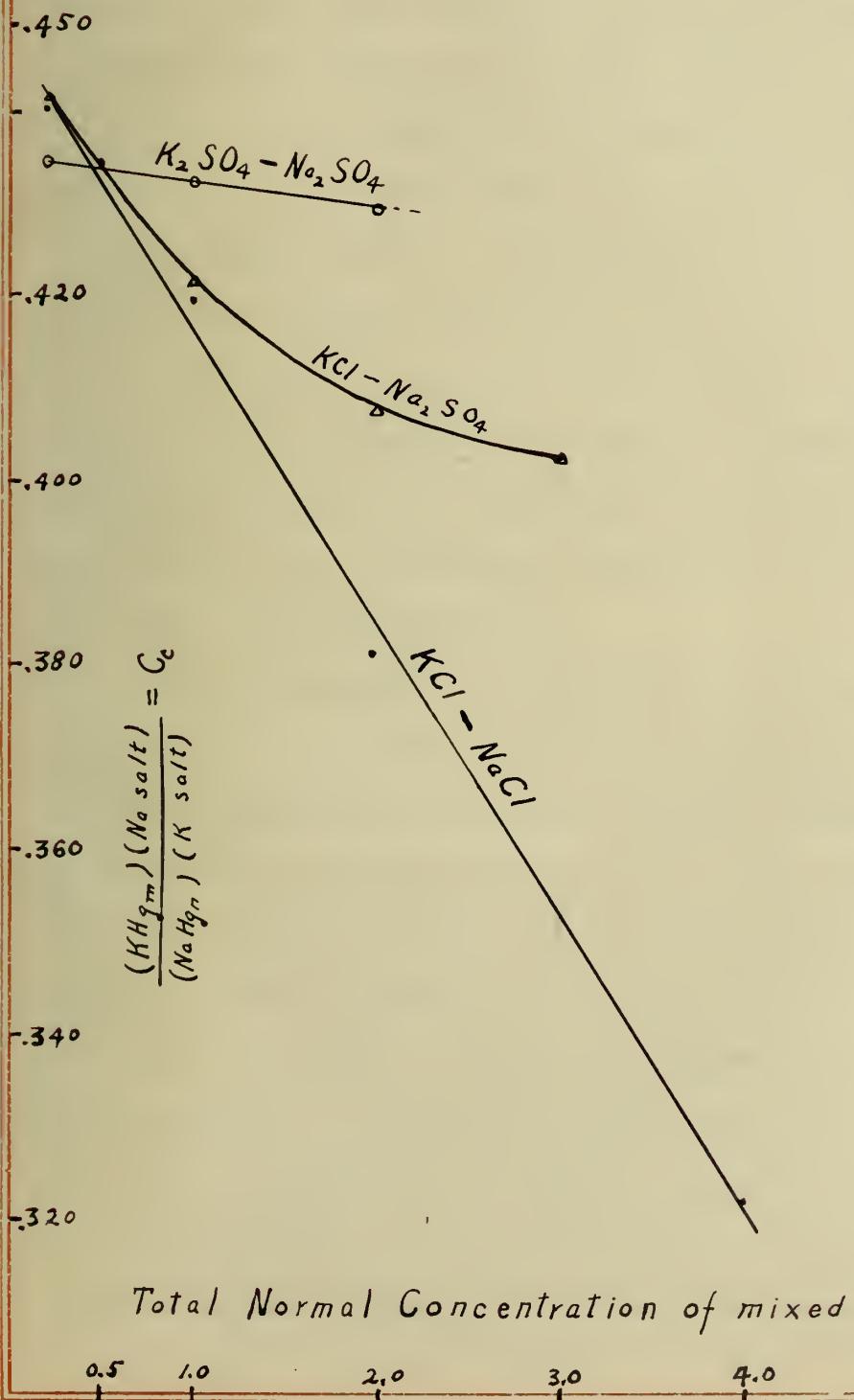
Np.	Normal concentration of salts.		Mol fract. in amalg, at start.	Wt. NaCl plus KCl	Wt. K <sub>2</sub> PtCl <sub>6</sub>	Mol fract. in amalg. at equilib.		C.	
	KCl	Na <sub>2</sub> SO <sub>4</sub>				KHg <sub>m</sub>	NaHg <sub>n</sub>		
1.	0.10	0.10		1.0	.2576	.3011	.3033	.6967	.435
2.	0.10	0.10		1.0	.2688	.3145	.3038	.6962	.438
3.	0.10	0.10		1.0	.2712	.3192	.3056	.6944	.440
4.	0.10	0.10	1.0		.2681	.3182	.3079	.6921	.445
5.	0.10	0.10	1.0		.2879	.3419	.3087	.6913	.446
6.	0.10	0.10	1.0		.3161	.3750	.3084	.6916	.446
							Mean	.441	
7.	0.50	0.50		1.0	.3169	.3617	.2957	.7043	.420
8.	0.50	0.50		1.0	.3413	.3886	.2950	.7050	.418
9.	0.50	0.50		1.0	.2930	.3353	.2964	.7036	.421
10.	0.50	0.50	1.0		.2870	.3283	.2966	.7034	.421
11.	0.50	0.50	1.0		.3318	.3791	.2962	.7038	.421
12.	0.50	0.50	1.0		.3162	.Lpst			
	NaCl	K <sub>2</sub> SO <sub>4</sub>					Mean	.420	
13.	0.50	0.50		1.0	.2983	.3397	.2949	.7051	.418
14.	0.50	0.50		1.0	.2964	.3388	.2962	.7038	.421
15.	0.50	0.50		1.0	.3202	.3658	.2960	.7040	.420
16.	0.50	0.50	1.0		.2913	.3334	.2966	.7034	.422
17.	0.50	0.50	1.0		.2929	.3380	.2992	.7008	.427
18.	0.50	0.50	1.0		.2979	.3395	.2952	.7048	.419
							Mean	.421	
19.	KCl	Na <sub>2</sub> SO <sub>4</sub>							
19.	1.0	1.0		1.0	.2935	.3280	.2889	.7111	.406
20.	1.0	1.0		1.0	.3121	.3482	.2884	.7116	.406
21.	1.0	1.0		1.0	.3015	.3372	.2894	.7106	.407
22.	1.0	1.0	1.0		.2885	.3223	.2890	.7110	.407
23.	1.0	1.0	1.0		.2955	.3303	.2890	.7110	.407
24.	1.0	1.0	1.0		.2872	.3229	.2899	.7101	.408
							Mean	.407	
25.	1.5	1.5		1.0	.2935	.3269	.2881	.7119	.404
26.	1.5	1.5		1.0	.2865	.3179	.2873	.7127	.403
27.	1.5	1.5		1.0	.3121	.3439	.2848	.7152	.398
28.	1.5	1.5	1.0		.2974	.3287	.2854	.7146	.400
29.	1.5	1.5	1.0		.2969	.3071	.2660	.7340	(.362)
30.	1.5	1.5	1.0		.2824	.3150	.2884	.7116	.405
							Mean	.402	

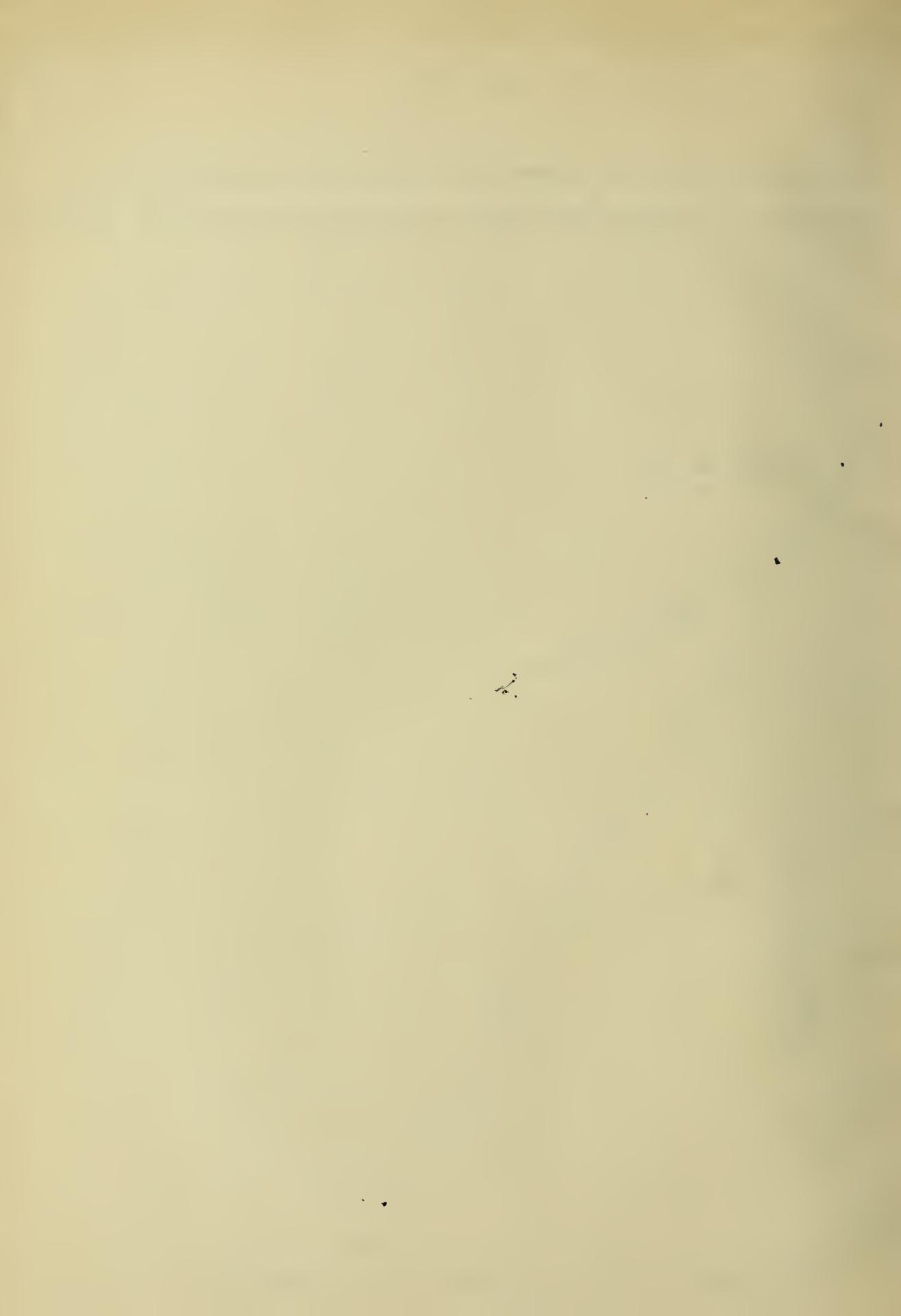
40 grams of 0.288% Na amalgam was used with 120 grams of mercury.  
 60 grams of 0.328% K amalgam was used with 100 grams of mercury.



FIGURE II.

Curves showing  $C_c$  as a function of the total concentration of mixed salts. The salts were used in equivalent quantities. Temp. 25° C.





complete data for the 0.20 normal solution have already been given in TABLE X, so only the mean value is shown here. The effect of increasing the total salt concentration is best studied by reference to the KCl-NaCl curve in FIGURE II, page 45, where the value of  $C_c$  has been plotted against the total concentration of the solution, using the data of TABLE XII. The dots mark the points determined experimentally with chloride-chloride mixtures. A straight line connecting the highest and lowest values of  $C_c$  passes very close to all of the other points determined; at 1.0 normal the observed value of  $C_c$  is slightly above the line and at 2.0 normal it is slightly below it, but in neither case is the deviation as great as 1.0% of the absolute value of  $C_c$  at that particular concentration. This is within the limits of experimental error, as can be seen from the data of TABLE XII; so we may conclude that, in the case of equivalent mixtures of sodium and potassium chlorides at 25°C, the value of the equilibrium constant,  $C_c$ , is a linear function of the total salt concentration.

(b)  $K_2SO_4$ - $Na_2SO_4$  - TABLE XIII, page 43, contains the data obtained upon increasing the total concentration of equivalent mixtures of sodium and potassium sulphates. Experiments 17 to 30 will be discussed later, together with Nos. 14 to 28 of TABLE XII. With the sulphate-sulphate mixture the value of  $C_c$  obtained from a 0.20 normal solution is .434. and from a 2.0 normal solution it is .429 - a decrease of only 1.1%; whereas, a similar change in the concentration of mixed chlorides reduces the value of  $C_c$  from .440 to .381. - a decrease of 13.4%. The sulphate-sulphate data are plotted in FIGURE II on page 45, where it is seen that the value of  $C_c$  is a linear function of the salt concentration, if it depends



upon it at all. The 1.1% decrease between 0.20 and 2.0 normal is so slight that it is of little significance, since some of the values of  $C_c$  at the higher concentration are higher than some gotten at the lower concentration. (Compare Nos. 2,3 and 4 with Nos. 35, 36,37 and 38 in TABLE XIII.)

## 2. Salts Without a Common Ion.

KCl-Na<sub>2</sub>SO<sub>4</sub>. - The effect of increasing the total concentration of equivalent mixtures of salts of two different types, with no common ion (KCl and Na<sub>2</sub>SO<sub>4</sub>), has been studied and the results are given in TABLE XIV, page 44. As a check upon the accuracy of the work, the solutions for experiments 7 to 12 were made by mixing equivalent quantities of KCl and Na<sub>2</sub>SO<sub>4</sub> and for Nos. 13 to 18 by mixing equivalent quantities of NaCl and K<sub>2</sub>SO<sub>4</sub>. As was to be expected, both combinations of salts gave substantially the same values for  $C_c$ . In this series an increase in the concentration of the salts causes a decrease in the value of  $C_c$ . Since on mixing KCl and Na<sub>2</sub>SO<sub>4</sub> there would result, by metathesis, two other salts, NaCl and K<sub>2</sub>SO<sub>4</sub>, one would expect to get a curve falling between the chloride-chloride and the sulphate-sulphate curves. If the metathesis,



were all that took place, one would also predict that the form of the curve would be the same as that of the other two; that is, that it would be a straight line. The chloride-sulphate data are plotted in FIGURE II, page 45. In this case the value of  $C_c$  is not a linear function of the concentration, but decreases at a constantly diminishing rate, until at 3.0 normal the effect of changing the concentration becomes very small indeed.



## CALCULATION OF THE ION FRACTIONS.

In the theoretical discussion (pages 5 to 9) an equation,

$$(K^+) = \frac{C_o (K \text{ salt})}{C_o (\text{Na salt}) + C_c (K \text{ salt})},$$

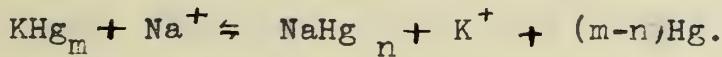
was developed, by which it is possible to calculate the ion fractions of the sodium and potassium at any particular concentration from the data of TABLES XII, XIII and XIV. Since all of the cases under consideration, the salts were present in the mixtures in equivalent quantities, the above formula reduces to the simple form,

$$(K^+) = \frac{C_c}{C_o + C_c}.$$

By extrapolating to zero concentration on the curves of FIGURE II, page 45, it is possible to obtain the value of the equilibrium expression,

$$\frac{(KHg_m) (Na^+)}{(NaHg_n) (K^+)} = C_c;$$

that is, to find the true equilibrium constant for the reversible ionic reaction,



Extrapolation on the chloride-chloride and the chloride-sulphate curves gives a value of .448 for  $C_o$ . By substituting this value, together with the values of  $C_c$  from the tables, in the above simple equation, the values of the ion fractions which exist in the various mixtures are readily obtainable. The data for the chloride-chloride and the chloride-sulphate mixtures are given in TABLE XV. on page 49.

The ion fraction of the potassium in the chloride-chloride mixtures decreases from 0.500, in an infinitely dilute solution, to

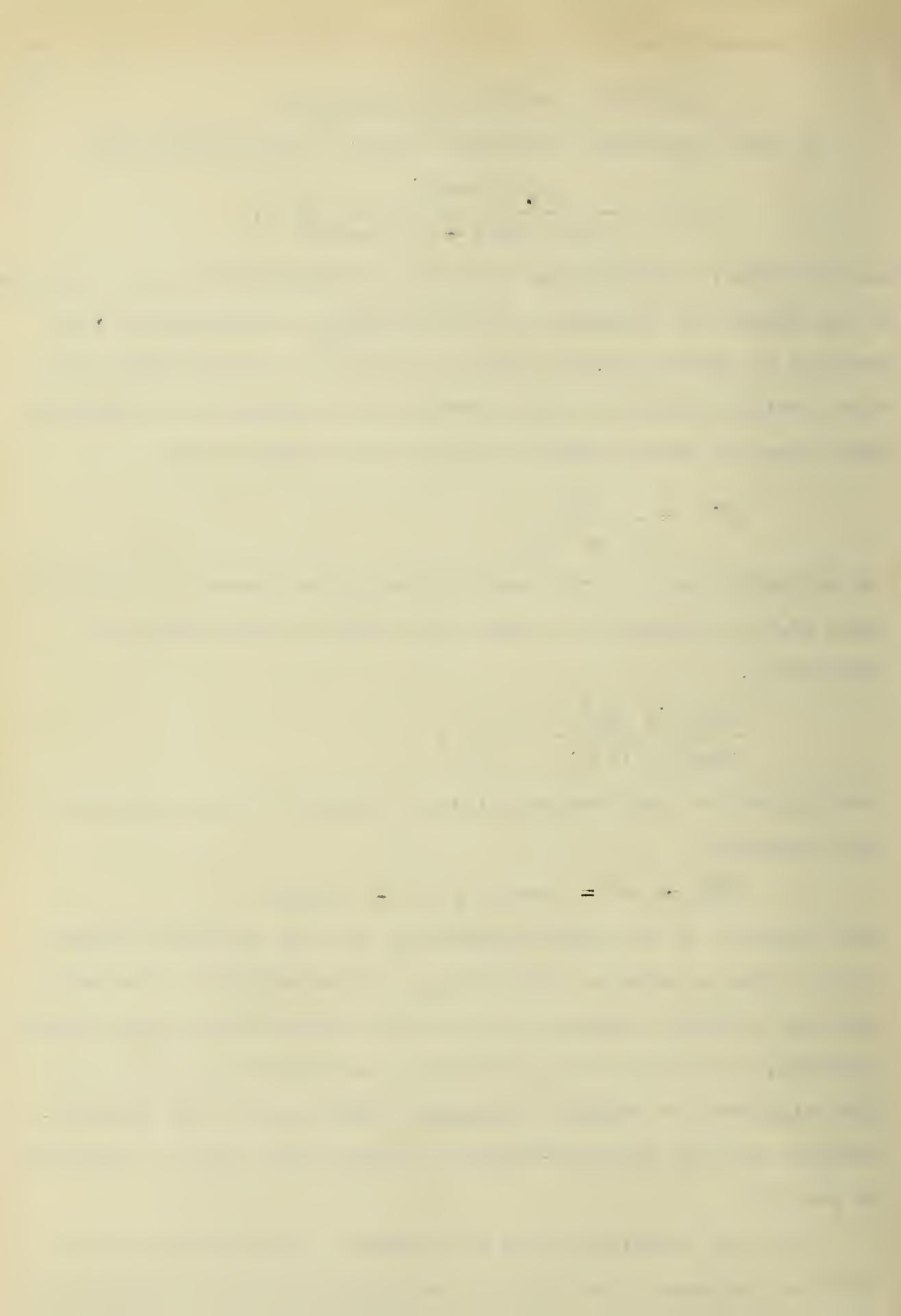


TABLE XV.

## Calculation of the Ion Fractions at 25°C.

Normality of salts in sol.		Total Normality	C <sub>O</sub>	C <sub>C</sub>	Calculated Ion Fractions	
KCl	NaCl				K	Na
0.00	0.00	0.00	.448	.448	.500	.500
0.10	0.10	0.20	" "	.440	.495	.505
0.25	0.25	0.50	" "	.434	.492	.508
0.50	0.50	1.00	" "	.419	.483	.517
1.00	1.00	2.00	" "	.381	.459	.541
2.00	2.00	4.00	" "	.322	.419	.581
KCl		Na <sub>2</sub> SO <sub>4</sub>				
0.00	0.00	0.00	.448	.448	.500	.500
0.10	0.10	0.20	" "	.441	.496	.504
0.50	0.50	1.00	" "	.420	.484	.516
1.00	1.00	2.00	" "	.407	.476	.524
1.50	1.50	3.00	" "	.402	.473	.527

.419 in a 4.0 normal solution; while in the chloride-sulphate mixtures the fraction decreases from .500 at zero concentration to .473 at 3.0 normal. The values of the ion fractions are plotted against the total concentration of the salt solution in FIGURE III, page 50. In the chloride-chloride curve the ion fraction appears to be a linear function of the concentration of the salts. If C<sub>C</sub> is a linear function of the salt concentration (FIGURE II), the ion fraction, calculated from the equations,

$$(K^+) = \frac{C_C}{C_O + C_C} \quad \text{and} \quad (Na^+) = 1 - (K^+) ,$$

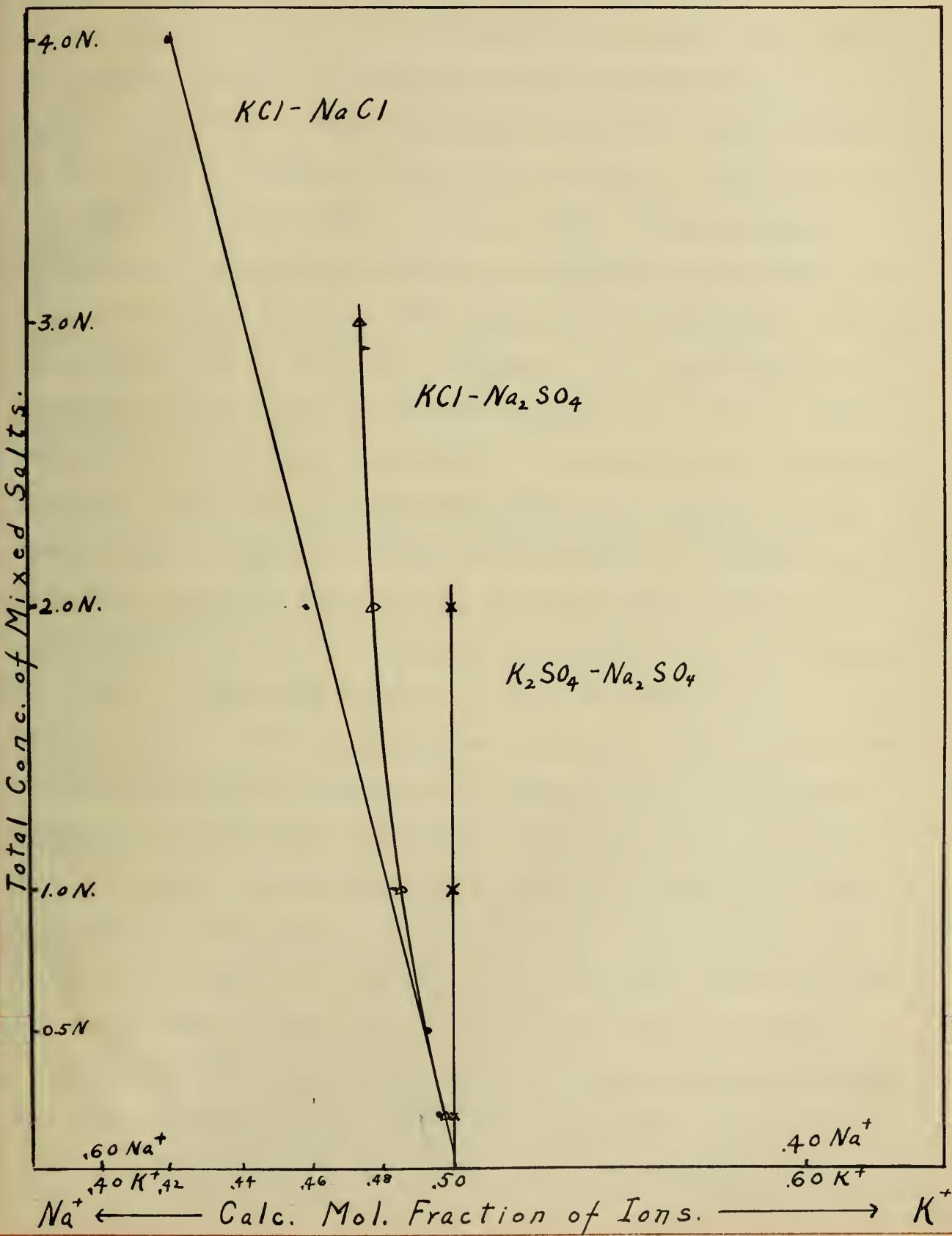
would not, theoretically, determine a straight line when plotted against the total concentration of the salts. Since, however, only a very small change in the ion fraction is produced (.500 to .419) the function may be considered linear over this small portion of the curve.

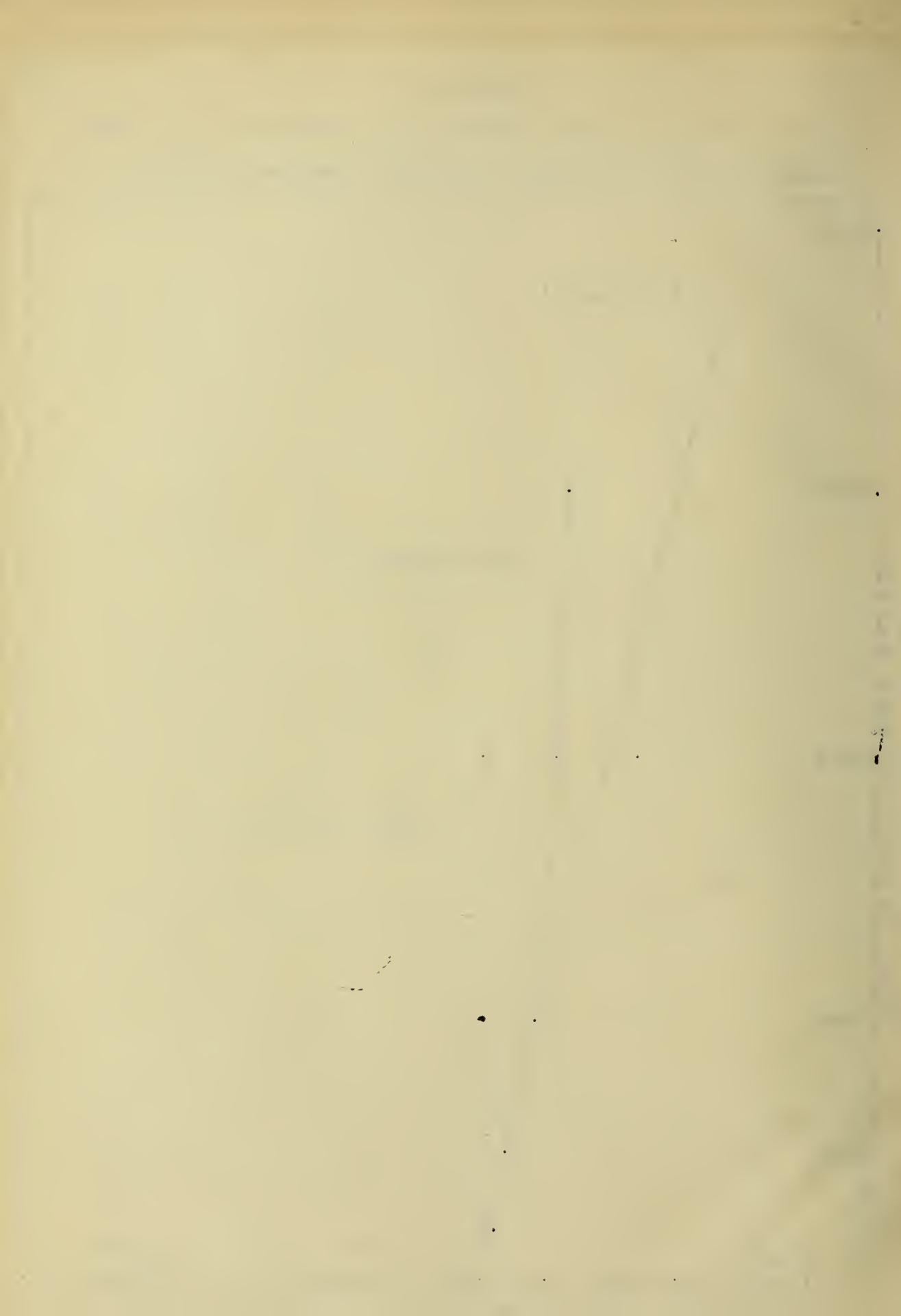
In the case of the chloride-sulphate mixtures, the curve has



FIGURE III.

Curves showing the Ion Fractions as a Function of the Total Concentration of the Salt Solutions. Temperature 25°C.





the same general form as that in FIGURE II, page 45. The potassium ion fraction decreases at a diminishing rate as the salt concentration increases.

In calculating the ion fractions of the sodium and potassium in the sulphate-sulphate mixtures, we are confronted with the difficult task of assigning a value to  $C_o$ , from the data at hand. Extrapolation on the curve of FIGURE II will give a value of .434 for  $C_o$ ; whereas, the other two curves gave a value of .448. Theoretically, an equivalent mixture of any two sodium and potassium salts should give the same equilibrium constant when each salt in the mixture is completely ionized; i.e. at infinite dilution. It is possible that the sulphate-sulphate curve in FIGURE II, page 45, may take a different form below 0.20 normal and actually cut the axis at a point that is common to the other two curves, but that would require a more abrupt change than we should feel inclined to assume. It might possibly seem that the whole curve should be raised by 0.014, so that it would terminate at .448 instead of at .434; but the concordance of the data in TABLE XIII renders it very improbable that an experimental error of this magnitude has been made. Each of the three points on the curve represents the mean of eight independent experiments, in which the equilibrium was approached from both sides, and in no case did the value of  $C_o$  differ from the mean value of the series by more than 1.6%; in most cases the agreement was within 1.0%. In the light of these facts, it is probable that the results are very nearly correct for the conditions which prevailed.

The difference in the values of  $C_o$  in the sulphate-sulphate and the chloride-sulphate mixtures at 0.20 normal cannot be attributed to a difference in concentration of the amalgams; as a matter



of fact the amalgams were identical. In the former series (see TABLE XIII) the mean weight of mixed chlorides obtained from the amalgams was 0.2725 gram, while in the latter series (see TABLE XV) it was 0.2783 gram.

All that we can justly say is that from 0.20 normal to 2.0 normal the value of  $C_c$  decreases by little more than 1.0%, and that the ion fractions of the sodium and potassium are practically constant over that range. This has been represented in FIGURE III by drawing a line almost vertically from the point 0.500 on the ion fraction axis. This at least serves to show the relative effect of changing concentrations upon the ion fractions of sodium and potassium in the three series of mixtures studied.

#### THE EFFECT OF CHANGING THE MOLFRACIION OF THE SALTS IN SOLUTIONS WHOSE TOTAL CONCENTRATION REMAINS CONSTANT.

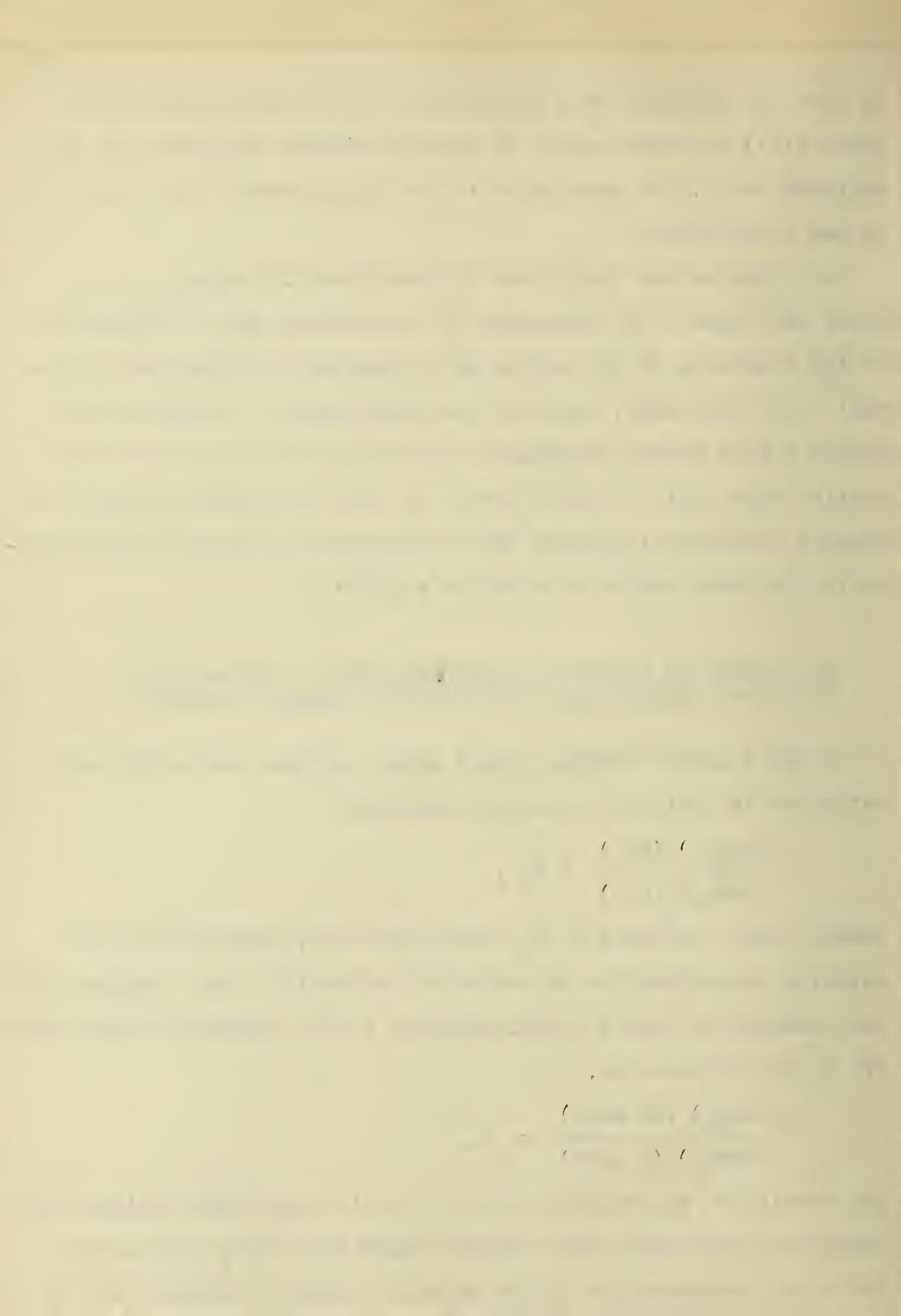
If the reaction between alkali metal amalgams and alkali salt solutions is ionic, the mass law expression,

$$\frac{(KHg_m) (Na^+)}{(NaHg_n) (K^+)} = C_o,$$

demands that the value of  $C_o$  remain constant, regardless of the relative concentrations of sodium and potassium ions. Assuming that the reaction is wholly ionic, constancy is not demanded in the value of  $C_c$  in the equation,

$$\frac{(KHg_m) (Na \text{ salt})}{(NaHg_n) (K \text{ salt})} = C_c.$$

The results of experiments carried out with undiluted amalgams, and recorded in the first four tables (pages 25 to 28), show that, if the total concentration of the solution remains constant,



the value of  $C_c$  is constant even though the mol fractions of the two salts in the mixtures vary over wide limits. The chloride-chlorides mixtures had a total concentration of 0.20 normal (see TABLE I page 25), and the relative salt concentrations varied from four parts of NaCl to one of KCl, to four of KCl to one of NaCl. In the experiments recorded in TABLES II to IV the total concentration of each mixture was 0.60 and the ratio between the salt concentrations varied from five to one, to one to five; but no appreciable variation in the value of  $C_c$  was observed.

When diluted amalgams and more concentrated aqueous solutions were used a slight change in the value of  $C_c$  could be observed as the ratio of the salt concentrations was varied. It was thought that at higher total salt concentrations, the magnitude of any variation which a change in the ratio might produce would be likely to increase. TABLE XII, page 42, contains the results obtained with dilute amalgams and solutions whose total concentration was 2.0N. Experiments 14 to 21 were carried out with a solution which was 1.666 normal with respect to KCl and 0.333 normal with respect to NaCl. The mean value of  $C_c$  from seven determinations is .383; whereas, experiments 22 to 28, in which the concentrations of the respective salts in the mixture were reversed, give a mean of .376. The difference between these values is less than 2.0%, and since the limits of accuracy with which each value can be determined is about 1.0%, no great significance can be attached to the difference at the present time.

Similar data for mixtures of sulphates at a total concentration of 1.0 normal are given in experiments 17 to 30 of TABLE XIII on page 43. Experiments could not be carried out at 2.0 normal, as was



done with the chlorides, because of the insufficient solubility of potassium sulphate. Experiments in which the aqueous solution was 0.833 normal with respect to  $K_2SO_4$  and 0.166 normal with respect to  $Na_2SO_4$  gave a mean value of .434 (Experiments 17 to 22), while the reverse mixture gave a mean of .423 (Experiments 23 to 30). The difference, while larger than was observed with the chloride-chloride mixtures, is still so slight that it is not considered conclusive. However, in both the chloride and the sulphate mixtures, an excess of potassium salt produced the higher value of  $C_c$ . This agreement in the direction of the change, together with the fact that an equivalent mixture of the salts, in both chloride and sulphate solutions, yields a value that is between those obtained with excess of potassium and excess of sodium salts, makes it seem likely that the change may be significant. By varying the ratio over still wider limits this difference, if real, should be magnified; this point will be taken up in a future investigation.



## V DISCUSSION OF THE RESULTS.

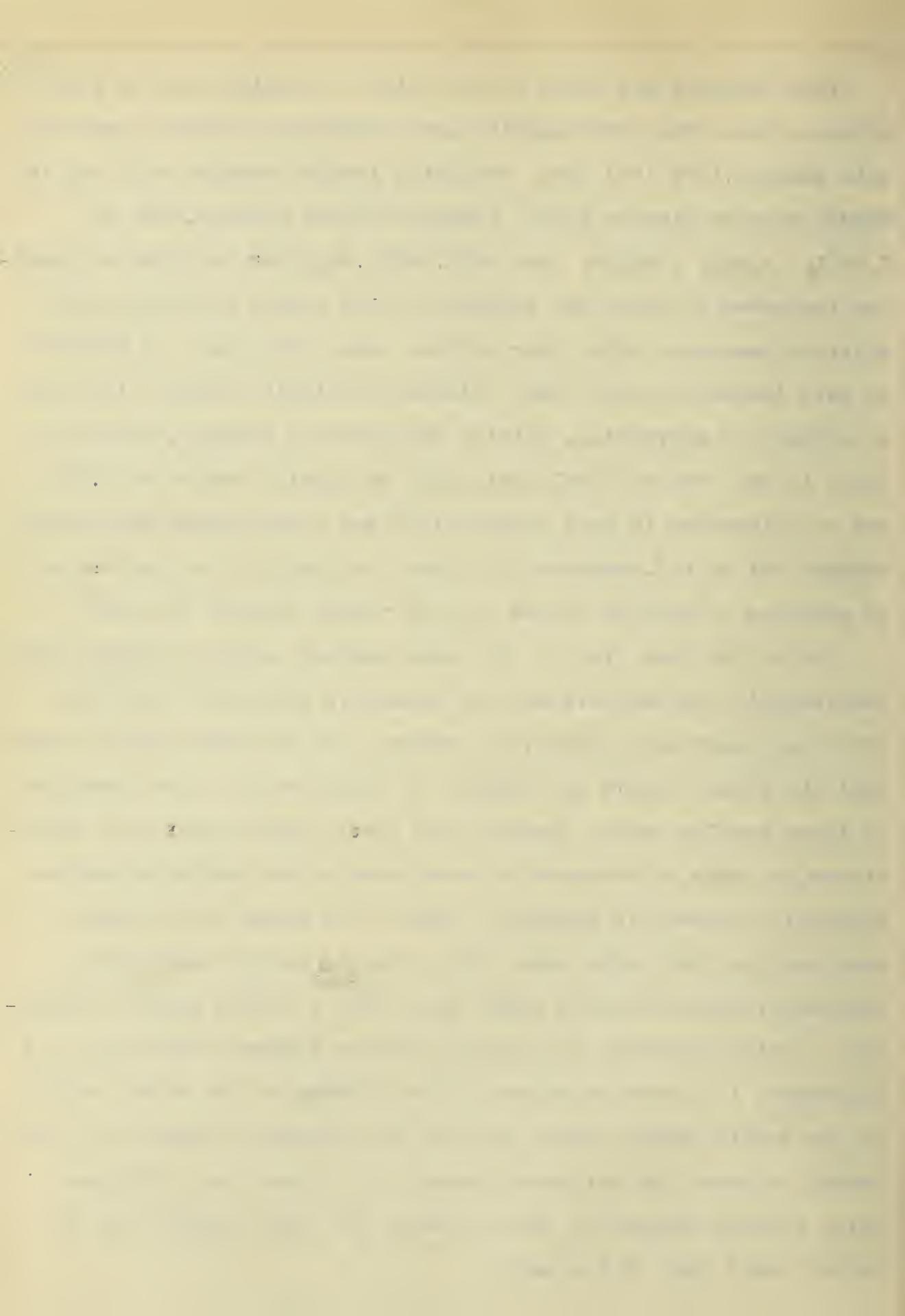
This study has shown, that, in equivalent mixtures of the chlorides, and of the chlorides and sulphates of sodium and potassium, the ion fraction of the potassium decreases with increasing total salt concentration; but that in the case of equivalent mixtures of the sulphates, at total concentrations ranging from 0.20 to 2.0 normal, the ion fractions are almost, if not quite, independent of the total salt concentration of the solution. This is in agreement with the results obtained by G. McP. Smith (1) on the chloride-chloride mixtures. The phenomenon is anomalous in view of the fact that, assuming the correctness of conclusions derived from the conductance data, potassium salts are slightly more highly ionized than the corresponding sodium salts, and we should, therefore, expect the same relations to exist in the mixture. G. McP. Smith (1) has made use of A. Werner's Theory of Higher Order Compounds to account for this apparent anomaly. According to this theory, the alkali halides should be capable of forming addition compounds with other substances and with one another; and in support of this assumption the following evidence is introduced.

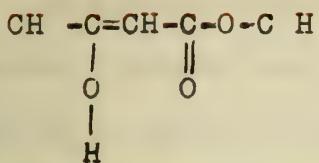
The recent introduction of the methods of "thermal analysis" into the field of organic chemistry has brought to light the fact that the property of forming addition compounds is characteristic of a great many substances and has even led some chemists to the belief that no chemical reaction takes place except through the preliminary formation of intermediate addition compounds. This property of forming addition compounds with other substances is ascribed by Werner (23) to all substances except the saturated hydrocarbons.



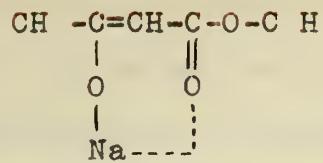
Alkali halides are known to add water in solution and to yield hydrated ions. They are capable also of forming addition compounds with ammonia.(24) (25) (26). Potassium iodide combines with  $\text{SO}_2$  in liquid sulphur dioxide.(26a) Numerous double halides, such as  $\text{K}_2\text{PtCl}_6$  ,  $\text{K}_2\text{HgI}_4$  ,  $\text{Na}_3\text{AlF}_3$  , and  $2\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , may be cited as familiar instances in which the tendency of the alkali halides to form addition compounds with other halides comes into play. In addition to this tendency to add other halides, the alkali halides also show a tendency to polymerize. Lithium chloride, for example, appears to exist in the form of double molecules in glacial acetic acid,(27) and to polymerize in amyl alcohol,(28) and transference experiments carried out by E.W.Washburn (29), point strongly to the existence of polymers of caesium iodide in 0.50 normal aqueous solution.

During the last five or six years Hantsch and his students have published, in the Berichte and the Annalen, a great many articles which are based upon absorption spectra data and which tend to show that the alkali metals are capable of taking part in the formation of inner complex salts. Hantsch (30, finds that the metallic derivatives, or salts, of acetoacetic ester show a very marked selective absorption, whereas in hexane, in which it is known to be highly enolized, the free ester shows only a feeble general absorption. Similarly, ethoxy-crotonic ester shows only a feeble general absorption. This difference in optical behavior Hantsch attributes to a difference in structure, caused by the linking of the alkali metal to the double bonded oxygen atom of the carboxyl, by means of a secondary valence. The following formulas will show the difference which Hantsch assumes to exist between the enol form and the so-called "aci" form of the salt.



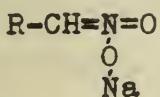


Enol form.

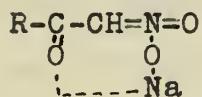


"Aci" form.

In a study of the nitro compounds, Hantsch and Voigt (31, have found, by the same method, that the salts of "conjugated" nitro compounds differ optically, and therefore structurally, from the salts of the simple nitro compounds. This difference they also attribute to a secondary valence linkage, as is shown in the following formulas:



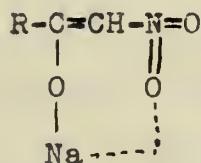
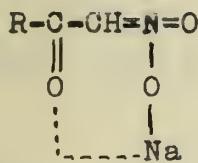
Simple "aci" nitro compound.



"Conjugated" aci nitro compound.

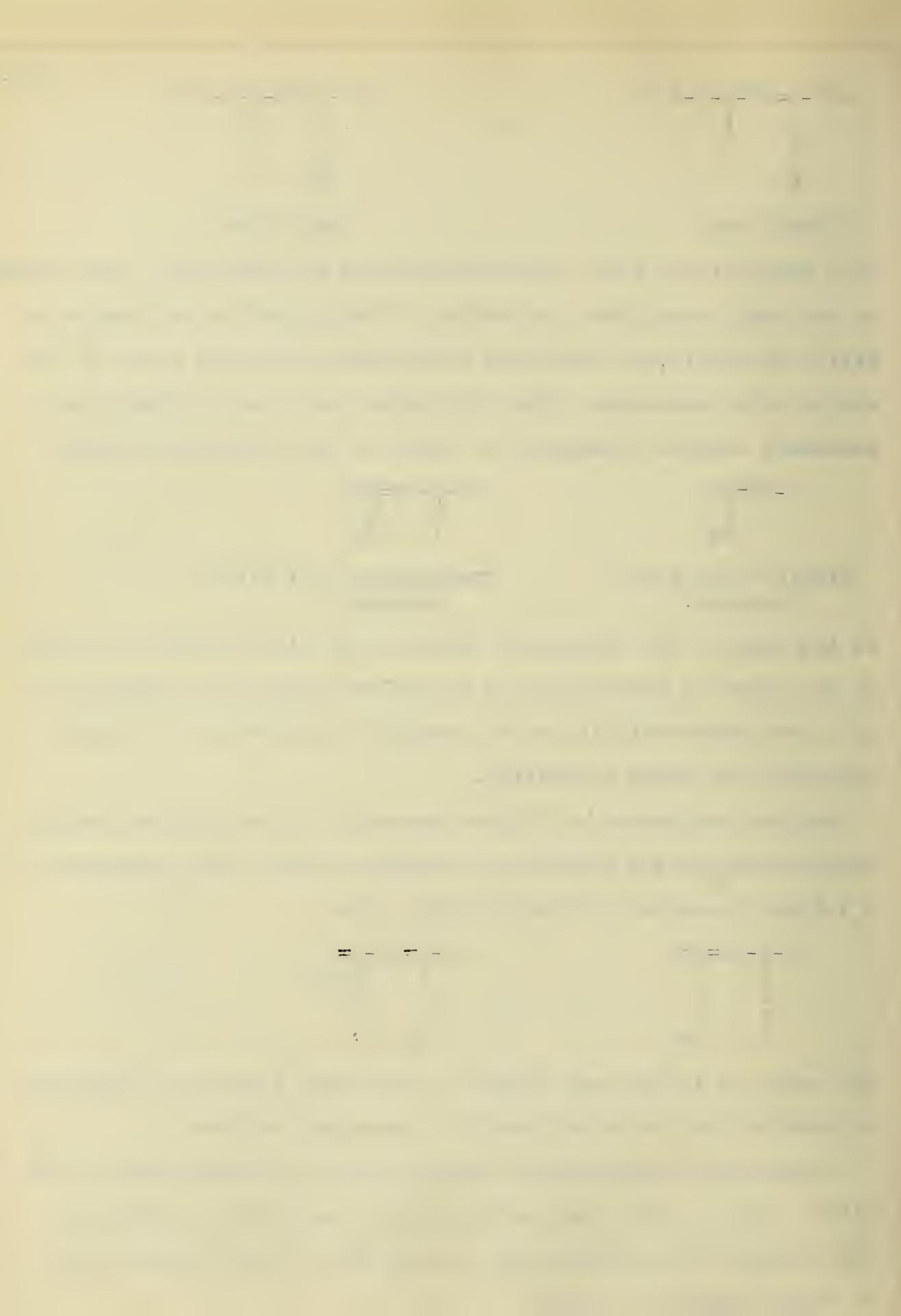
In the case of the conjugated compound the alkali metal is joined to the negative substituent of the molecule, with the formation of a ring compound; this is not possible in the case of a simple unsubstituted nitro derivative.

Certain conjugated "aci" nitro compounds of the alkalies exhibit chromoisomerism, and Hantsch and Voigt attribute this phenomenon to a valence isomerism of the following type:



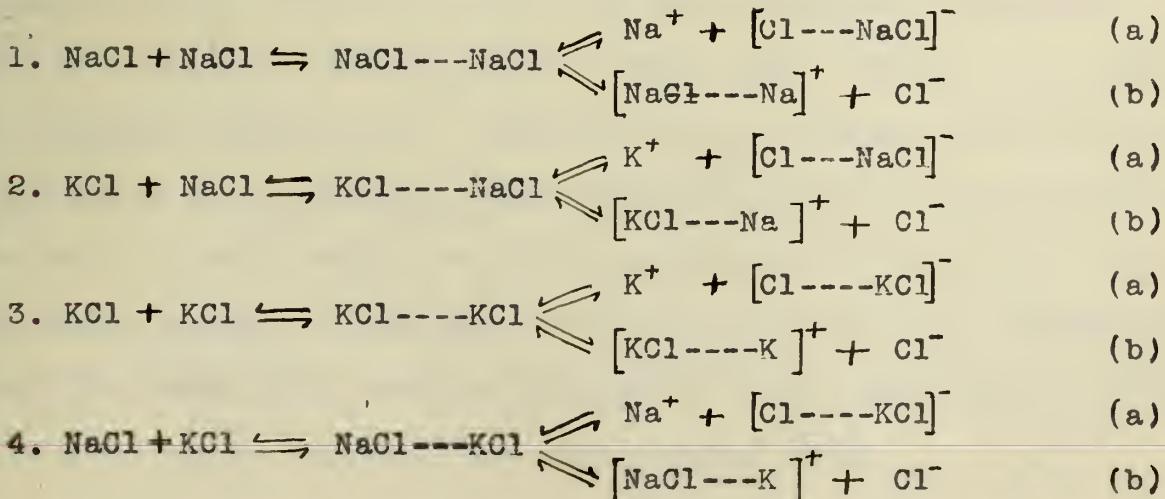
The metal is in one case linked to the nitro group by a principle valence and in the other case by a secondary valence.

Conductance measurements carried out by Lifschitz (32) on the alkali salts of the oximino-ketonic and the nitrolic acids, have led him also to conclude that in some cases inner complex salts of these metals are formed.



In a very recent study, C. Sandonnini (33) has carried out conductance measurements with mixed sodium and potassium chloride solutions, in which he finds that the experimentally obtained values are somewhat lower than the calculated values. The original article is not available and the abstract does not make it clear whether he concludes that this difference indicates the formation of a complex or not. Sandonnini finds that the sodium chloride-sodium sulphate mixture studied has a conductance which is 2.2% lower than the calculated value; while solutions in which complexes are known to exist have conductances that are but seven or eight percent lower than the calculated values; the pair  $KCl-HgCl_2$ , at 5 mol percent of  $KCl$ , gives a difference of only 7%. If a decrease in conductance is taken to indicate the presence of complexes in the solution, it would seem that they should be present in a considerable extent in the  $NaCl-Na_2SO_4$  mixture, and not altogether lacking in the  $NaCl-KCl$  mixture.

Assuming, then, that the alkali metal halides may polymerize or combine with one another in aqueous solution to form higher order compounds, we have in the case of mixed sodium and potassium chloride solutions, the following possible types of equilibria:





The broken lines indicate secondary valence linkages, as suggested by Werner. For the sake of simplicity, compounds which may possibly be formed with more than two molecules of alkali halides, have not been represented in the equilibria.

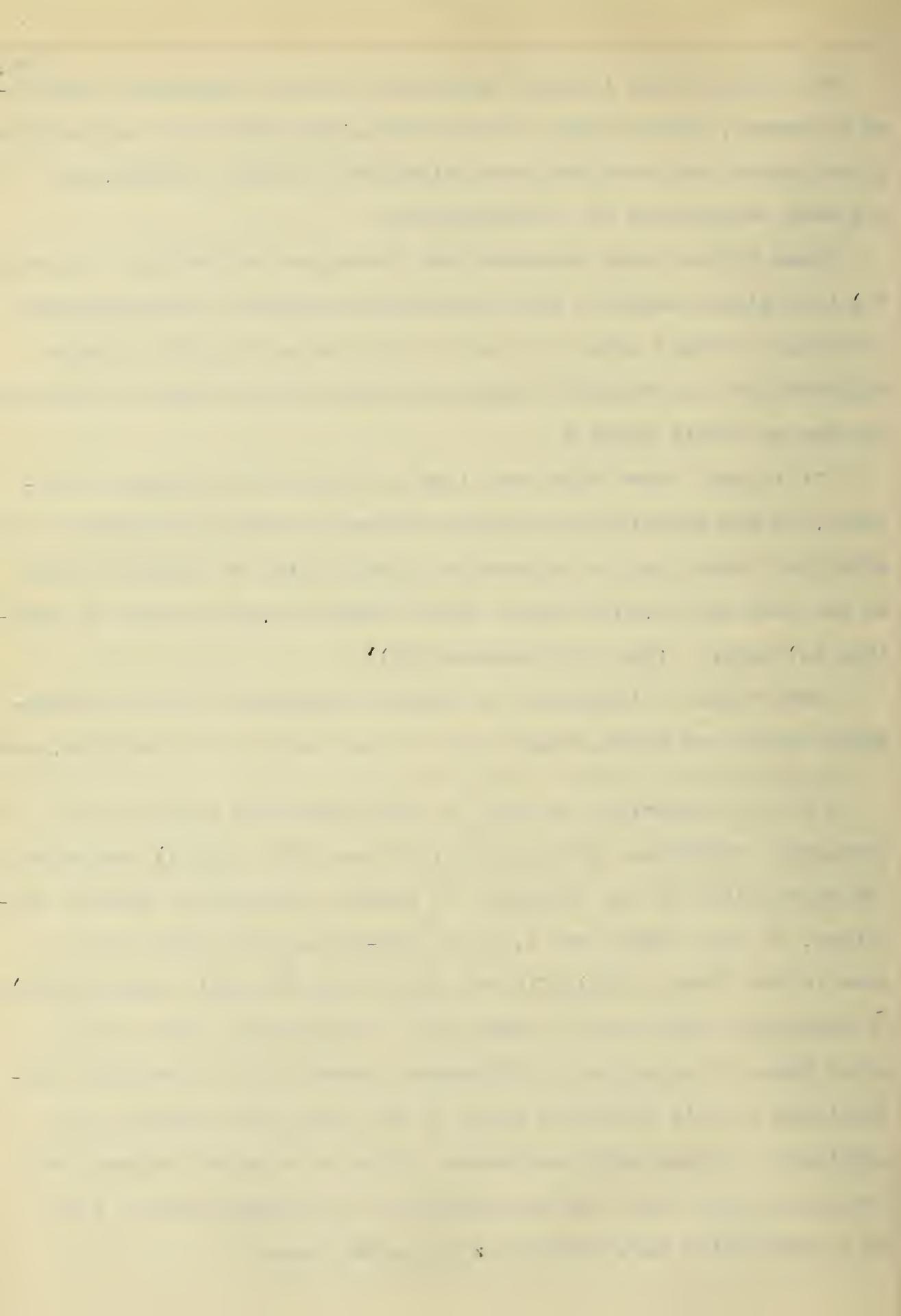
These higher order compounds may ionize, as indicated, in two ways: (a) into simple metallic ions and complex negative ions, containing one atom of alkali metal and two of chlorine, and (b, into simple chloride ions and positive complexes containing one atom of chlorine and two of alkali metal.\*

It is well known that most ions are hydrated in aqueous solutions. If the equilibria represented above do exist, the complex ions which are formed may be regarded as alkali metal or chloride ions, as the case may be, which carry alkali halide instead of (or in addition to) water. [See E.W. Washburn, (29)].

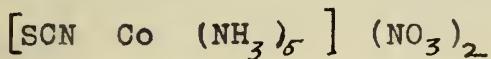
Both forms of ionization of complex compounds which are represented above are known. Nearly all of the stable double halides, such

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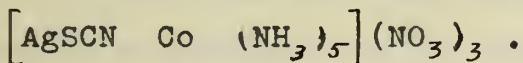
\* It is interesting to note in this connection that, as early as 1893, Meijer Wildermann [Berichte 26, 1773 and 2881 (1893)] recognized the possibility of the formation of double molecules in aqueous solutions. He says, "Haben wir z.B. eine ClK-Lösung, und nehmen wir an, dass in der Lösung  $(ClK)_2$ , ClK, und ihre Ionen  $ClK_2^+$ ,  $Cl^-$  (resp.  $Cl_2^-K^+$ ),  $Cl^-$  vorhanden sind---etc." These ions are identical with the ones given above in equation 3. Wildermann discusses the electrical conductivity of salt solutions which do not follow the dilution law applicable to weak acids and bases, and by an extended mathematical treatment shows that such an assumption is in accordance, at least in a qualitative way, with the experimental data.



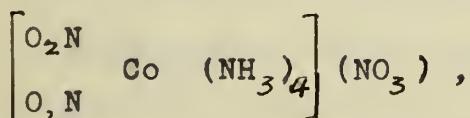
as  $K_2PtCl_6$ , ionize, at least primarily, to give a simple metallic ion and a complex ion containing all of the halogen. This is in accordance with the scheme of ionization represented above under (a). On the other hand, Werner (loc. cit. pp. 304-309), discusses certain complex cobalt salts which ionize according to the second scheme, (b). Thiocyanato-pentammino-cobalti nitrate,



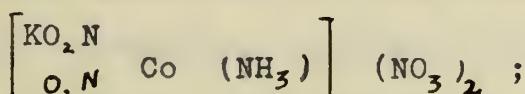
for example, will combine with silver nitrate in such a way as to give a tri-trivalent salt which contains both cobalt and silver in the complex, and which does not immediately give a precipitate with HCl; showing that the silver is in the non-ionic condition. Since the greatest number of groups which can be assembled around a cobalt atom is six (maximum co-ordination number), it must be assumed that the silver is directly combined with the thiocyanate radical, and that the compound has the structure represented by the formula,



The other properties of the compound are in complete harmony with this structural formula. Again, 1,2 dinitro-tetrammino-cobalti nitrate,

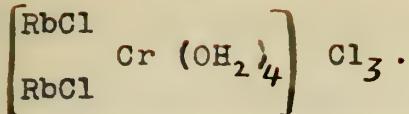


is capable of adding one molecule of  $\text{KNO}_3$  to form a crystalline salt, to which Werner assigns the formula,



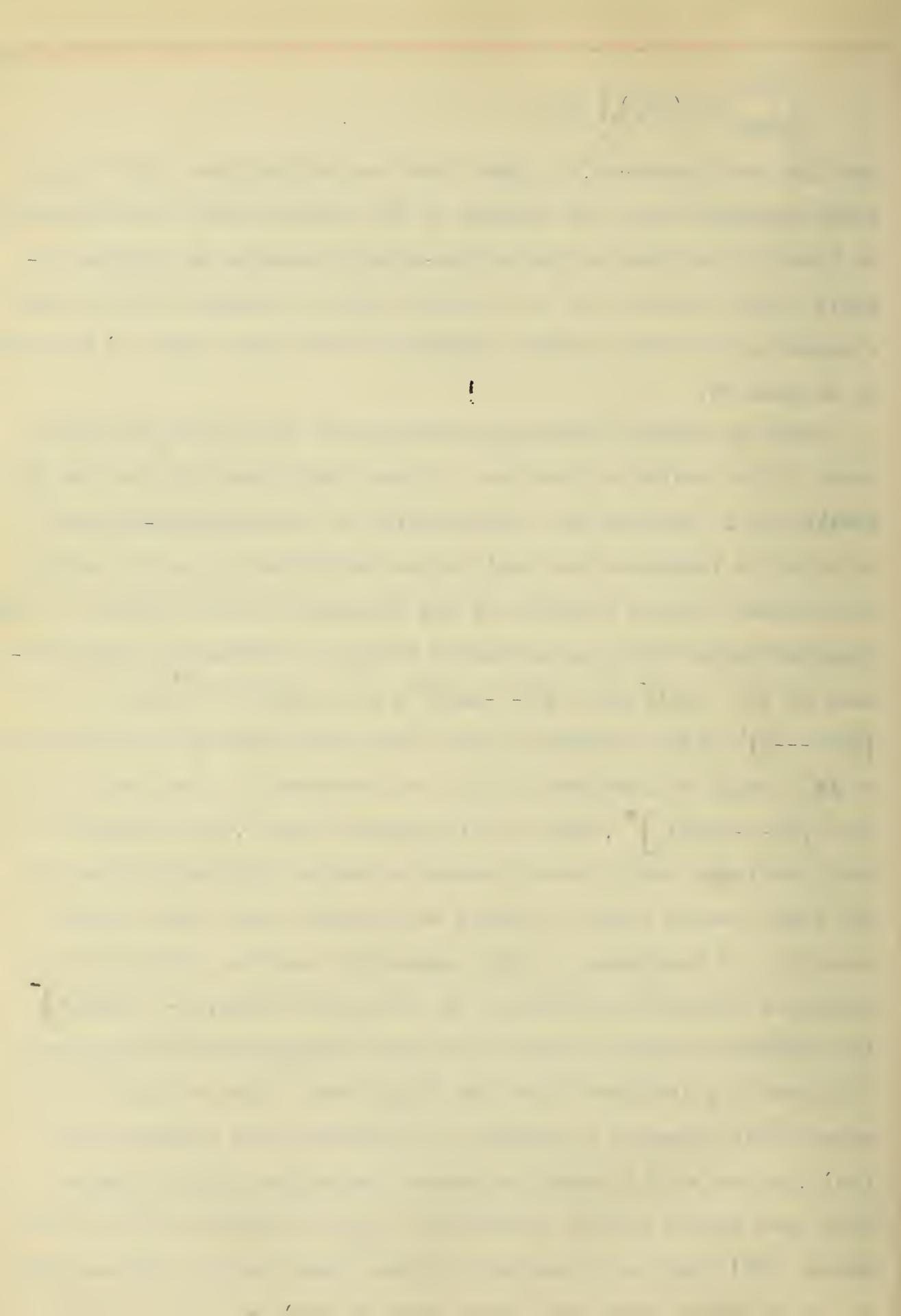
also an analogous chromium compound is listed by Werner, having the formula,





The last two compounds, to judge from the context, have their structures assigned purely by analogy to the silver-cobalti compound; but at least in the case of the silver-cobalti complex we have an example of the addition of an ionizable salt to another salt, in such a manner as to form a stable complex of the second type (b) referred to on page 58.

With our present knowledge, speculations as to just what ions exist in the solutions are more or less futile, and all that we can justly say is that as the concentration of the chloride-chloride solution is increased the equilibrium is shifted in such a way as to decrease the ion fraction of the potassium in the solution. The observed result might be accounted for by an increasing preponderance of  $[\text{Cl---KCl}]^-$  over  $[\text{Cl---NaCl}]^-$ ; or of  $[\text{KCl---K}]^+$  over  $[\text{NaCl---K}]^+$ , with increasing total salt concentration of the solution; or it might be accounted for by the presence of complexes of the form  $[\text{Na---(ClK)}_n]^+$ , where "n" is greater than 1. The formation of such complexes would remove potassium faster than sodium ions, but the final result would of course be dependent upon the relative stability of complexes of this composition and the corresponding complexes containing potassium as the central atom,  $[\text{K---(ClNa)}_n]^+$ ; the different values of "n" in the two complexes would also exert a determining influence upon the final result. The sodium ion is more highly hydrated in aqueous solution than the potassium ion (34), and we should therefore expect the sodium ion to combine with more alkali halide. Moreover, it has been pointed out by G.H. Hansen (35) that the elements with the lowest atomic volumes form the most stable complexes. Fritz Ephraim (36) has studied this

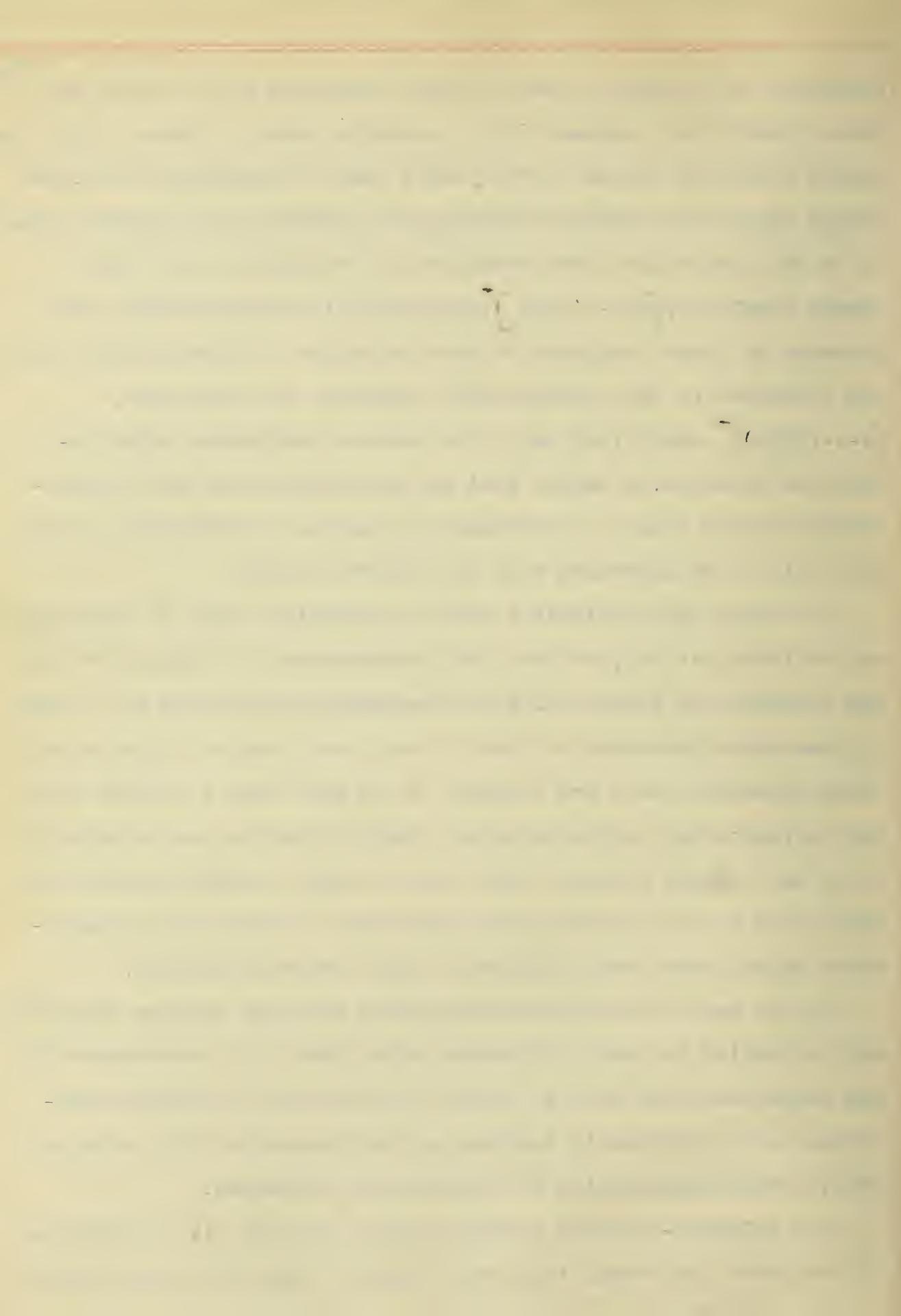


principle in the case of many of the hexammines and he finds that their stabilities increase with increasing atomic volumes. Since the atomic volume of sodium is 23.7, while that of potassium is 45.5, we should expect the complex containing the sodium as the central atom to be the more stable. The formation by the sodium ion of more stable complexes,  $[\text{Na---(ClK)}_n]^+$ , especially if connected with the presence in these complexes of more molecules of alkali halide than are contained in the corresponding potassium ion complexes,  $[\text{K---(ClNa)}]^+$ , would lead us, in the case of equivalent chloride-chloride mixtures, to expect that an increasing total salt concentration should lead to a decreasing potassium ion fraction. In any case this is in agreement with the observed facts.

Of course the possibility must be recognized that no complexes may be formed at all, and that the preponderance of sodium ions in the concentrated sodium and potassium chloride mixtures may be due to some other cause; but in view of the facts that in dilute solutions potassium salts are supposed to be more highly ionized than the corresponding sodium salts, and that the sodium ion is known to be more highly hydrated than the potassium ion, this possibility would seem to be, in reality, very improbable. Transference experiments might throw some additional light upon this subject.

In the case of the chloride-sulphate mixtures similar reasoning may be applied, the only difference being that the preponderance of any complexes which tend to lower the potassium ion fraction increases at a continually decreasing rate, instead of at a constant rate, as the concentration of the solution increases.

The sulphate-sulphate mixtures may or may not yield complexes. If complexes are formed they are of such a nature that they remove sodium and potassium ions at very nearly the same rate, since in



this case the ion fractions of the two metals are practically independent of the total concentration of the solution. The interaction of the two salts may result mainly in a simple metathesis, giving the mixed sodium and potassium sulphate,  $\text{NaKSO}_4$ , in which each metal is equally free to ionize. The data point to a slight complex formation, since  $C_c$  does decrease slightly as the salt concentration increases; but provided the relative stabilities of the compounds formed are in accordance with the above condition, the fact that the decrease of  $C_c$  is slight does not preclude the possibility of a very high concentration of complexes.

## VI SUMMARY.

Potassium amalgam forms supersaturated solutions in mercury. The true solubility, at the ordinary temperature, is about one-fifth of the published value.

The value of the mass law expression,  $C_c$ , for the equilibrium between sodium and potassium salt solutions and liquid sodium and potassium amalgams, is dependent upon the concentration of the amalgams. The effect of changing the concentration is very marked in the region of supersaturation.

The value of  $C_c$  is practically independent of the total concentration of equivalent mixtures of sodium and potassium sulphates up to 2.0 normal, at  $25^\circ\text{C}$ .

The value of  $C_c$  falls linearly with increasing total concentration of equivalent mixtures of sodium and potassium chlorides up to 4.0 normal, at  $25^\circ\text{C}$ . This decrease in value is in accordance with the data of G. McP. Smith, who worked with more concentrated amalgams.

The value of  $C_c$  falls with increasing concentration of equivalent mixtures of potassium chloride and sodium sulphate, at  $25^\circ\text{C}$ , but



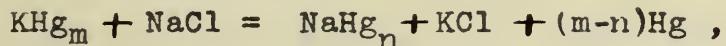
the decrease is not linear.

These results are interpreted as indicating the formation of complexes in the solutions.

A. Werner's theory of higher order compounds offers a plausible explanation of the nature of such complexes.

In the case of equivalent mixtures of sodium and potassium chlorides at a total concentration of 0.20 normal, the value of  $C_c$  decreases with increasing temperature between  $15^\circ\text{C}$ . and  $30^\circ\text{C}$ . Determinations were made at  $15^\circ$ ,  $20^\circ$ ,  $25^\circ$ , and  $30^\circ\text{C}$ .

The heat of the reaction,



is about -3000 calories.



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## VIII. Biography.

The writer of this thesis was educated in the public schools at Galva, Iowa. He received the degree of Bachelor of Science at Drake University in 1908, and the degree of Master of Science at the University of Illinois in 1914. During the academic year 1908-1909 he was a student in the Graduate School of Harvard University. Since 1909 he has held the following positions:

Instructor in Chemistry and Physics in the High School at Oskaloosa, Iowa. 1909-1910.

Instructor in Chemistry at Drake University, 1910-1913.

Assistant to the Chemist of the Iowa State Board of Health, 1910-1912.

Assistant in Chemistry at the University of Illinois, 1913-1915.

Fellow in Chemistry at the University of Illinois, 1915-1916.

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